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Canada Centre for Mineral and Energy Technology | Centre canadien de la technologie des minéraux et de l'énergie

SO_2 SORBENT UTILIZATION IN FLUIDIZED BEDS

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SO_2 SORBENT UTILIZATION IN ATMOSPHERIC FLUIDIZED BEDS

by

C.A. Hamer

ABSTRACT

The use of limestone and dolomite as sorbents for SO_2 emitted during the fluidized bed combustion of coal was investigated. The literature was reviewed to determine the factors which affect sorbent utilization and the methods reported to improve sorbent efficiency. Twenty-nine samples of limestone and dolomite from thirteen deposits in Nova Scotia, New Brunswick and Alberta were evaluated in a small fluidized bed test reactor. Samples were exposed to a synthetic flue gas containing 0.3% SO_2 at 850°C in a fluidized bed of sand. Twenty of the same samples were also evaluated by thermogravimetric analysis under contract. The results of the two methods are compared. The Argonne National Laboratory model was used to predict the performance of sorbents in the Combustion and Carbonization Research Laboratory's (CCRL) fluidized bed combustor (FBC) and also in the CFB Summerside FBC. Predicted limestone behaviour agreed very well with data from CCRL tests.

UTILISATION D'UN SORBENT DE SO_2 DANS LES LITS FLUIDISÉS

par

C.A. Hamer

RÉSUMÉ

On a examiné l'utilisation de calcaire et de dolomite comme sorbents du SO_2 émis pendant la combustion du charbon en lit fluidisé. On a étudié la documentation disponible pour déterminer les facteurs qui influent sur l'utilisation du sorbent et les méthodes permettant d'améliorer son efficacité. Vingt-neuf échantillons de calcaire et de dolomite provenant de treize dépôts en Nouvelle-Écosse, au Nouveau-Brunswick et en Alberta ont été évalués dans un petit réacteur d'essai. Les échantillons étaient exposés à un gaz de carneau synthétique contenant 0,3 % de SO_2, à 850°C, dans un lit fluidisé de sable. Vingt de ces mêmes échantillons ont aussi été évalués par une méthode thermogravimétrique dans le cadre d'un contrat. Les résultats des deux méthodes sont comparés. On s'est servi du modèle de l'Argonne National Laboratory pour prévoir la performance de sorbents dans le réacteur à lit fluidisé du Laboratoire de recherche sur la combustion et la carbonisation (LRCC) et la performance dans le réacteur du CFB Summerside. Le comportement prévu du calcaire concordait très bien avec les données obtenues lors des essais au LRCC.

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INTRODUCTION

CANMET has been involved with projects on atmospheric fluidized bed combustion (AFBC) of coal for several years. As an element of a project on fluidized bed combustion and emission abatement parameters, studies are being conducted on the utilization of Canadian limestone as sorbents for SO_2 emitted during FBC of coal. This work includes an investigation of methods to improve the efficiency of limestones to capture SO_2 and also a model to predict limestone requirements for large scale units from bench scale data. The limestones chosen for the initial investigative work were from locations with the greater potential use of FBC, that is, Nova Scotia and New Brunswick which have high sulphur coals, and near present and future tar sands plants in Alberta which produce a high sulphur byproduct coke.

The use of limestone or dolomite as sorbents to capture sulphur dioxide in fluidized bed combustion is a well established technology. In a fluidized bed combustor, coal and limestone are fed into an air-fluidized bed of calcined sorbent. The combustion of coal in the bed at 800° to 950°C evolves heat for thermal power generation or heating purposes. The sulphur associated with the coal is released as sulphur dioxide which reacts with the calcium oxide in the bed to form solid calcium sulphate:

$$CaO + SO_2 + \tfrac{1}{2}O_2 \rightarrow CaSO_4$$

Continuous removal of spent bed material and its replacement by fresh limestone maintains the desulphurization action of the bed.

Theoretically, one mole of calcium oxide is required for each mole of sulphur released during the combustion of coal. In practice however, a threefold or greater excess of calcium oxide is often required to capture 90% of the sulphur dioxide emitted. Thus in the FBC of a 5% sulphur coal, limestone requirements could vary from 0.5 to over 1.8 kg per kg coal. The difference between practice and theory, that is, the efficiency of the above reaction, is dependent upon a variety of parameters which affect the kinetics of this gas-solid reaction. Such parameters are gas residence time, temperature, gas composition, calcination conditions, sorbent particle size, grain size, porosity and chemical composition. The physical and

chemical properties of the sorbent can vary significantly from one source to another and can have a dominant effect on the efficiency of SO_2 capture.

This report will start by reviewing some of the technical literature on sorbent utilization in FBC in order to determine efficiency of capturing SO_2. A fluidized bed test reactor was built to evaluate limestones and dolomites under conditions simulating full scale fluidized bed units. The results of the reactor tests are compared with the more commonly used thermogravimetric analysis method. Twenty-nine samples were tested in the fluidized bed reactor and nineteen of the same samples werre evaluated by TGA. For a number of quarries and deposits samples were taken at different time periods and locations within the deposit to evaluate the consistancy of the limestone. The sulphation capacity, or the per cent conversion of $CaCO_3$ to $CaSO_4$, found in these test methods permits the identification of the better sorbents. However, a more definitive ranking of sorbents is obtained by using the test sulphation data in a model which predict the performance of sorbents in large scale FBC units. A computer program for the model and the predicted behaviour of all the sorbents in the Summerside FBC unit are given in the report. Having determined an evaluation method for SO_2 sorbents and the behaviour of these sorbents a future report will investigate methods to improve their efficiency.

FACTORS AFFECTING THE UTILIZATION OF LIMESTONE

LIMESTONE AND DOLOMITE

In fluidized bed coal combustion the common sorbent for capturing SO_2 is CaO, which is introduced into the combustor as limestone, $CaCO_3$ or dolomite, $CaMg(CO_3)_2$. Although the magnesium in dolomite takes little part in the reaction with SO_2 at the fluid bed operating temperatures, dolomites have been reported to be more reactive than limestone such that the calcium utilization can be very high and this can compensate for its lower content.

Limestones are sedimentary rocks formed mainly through the deposition of calcareous material on ancient sea bottoms or in similar depositional basins. It can vary from almost pure calcite, e.g., marble, to a variety of other minerals such as aragonite and chalk depending upon the composition of the original calcareous material, the conditions of metamorphism and the

elements or materials added from adjacent rock masses or igneous sources.

The chemical composition of limestones are principally calcium oxide, CaO, and carbon dioxide, CO_2. Magnesium oxide, MgO, is a common constituent. It substitutes for calcium oxide as a result of transformation of limestones by magnesium-bearing solutions. The amount of substitution can vary up to the composition of dolomite, $CaMg(CO_3)_2$. Small amounts of silica and alumina may be present as a result of the presence of clastic materials, quartz and clay. Iron oxide may be present, either as carbonate or in other minerals such as clays. Additionally there will be a host of trace elements. There is thus a great variety of material which is commonly called limestone, and it varies in physical properties and chemical composition from deposit to deposit and even within the same deposit. These properties have a significant influence on the behaviour of a limestone as a sorbent for SO_2.

PHYSICAL CHARACTERISTICS OF SORBENTS

The physical properties of pore volume and size combined with particle size are the outstanding determinants of sorbent activity (1). In the reaction of SO_2 with CaO, $CaSO_4$ forms on the surface and in the pores of the calcined limestone. Because the molar volume of $CaSO_4$ (52.2 cm^3/g mole) is greater than that of CaO (16.9 cm^3/g mole) or $CaCO_3$ (39.9 cm^3/g mole), the reaction product essentially seals the surface and fine pores and retards further reaction of SO_2 with the unreacted lime core. A limestone with a large pore volume made up principally of pores, whose diameter is greater than 0.08 μm after calcining, has a much greater SO_2 capacity than a stone with a small pore volume composed of narrow mouth pores (2,14). Small pores facilitate high initial reaction rates, but plug rapidly giving overall low capacities especially with large particle-size stones. Large pore stones sulphate at a slower rate but give greater overall capacity. Obviously the smaller the particle size the greater is the surface area and exposed pore volume and the more complete is the limestone utilization. It is the pore size of the calcined stone which is the important parameter rather than that of the raw stone.

Harvey (3) investigated the influence of the petrographic properties of carbonate rocks on the sorption of SO_2. He found that the finer the grain

size of the rock, the higher the sorption capacity. However, the fine-grained, dense, limestones depart from this trend and have unusually low capacities. This work was done in a fixed bed reactor at 980°C.

Munzner (4) compared a number of European stones in a 6 cm dia fluid bed unit and concluded that next to purity, that is calcium content, porosity is the most important parameter influencing sulphur capture. He also confirmed the findings of others that on a Ca/S basis dolomites are usually more effective than limestones. As a rough rule-of-thumb, the older the geological age of the stone, the lower its porosity and sulphur capture capacity. Potter's results (5) indicated that chalks had the best reactivity followed by oolite, dolomite and calcite in that order. His samples were calcined at 980°C which is a somewhat higher temperature than that which atmospheric fluid beds normally operate. Both Borgwardt and Harvey (6) and Spitsbergin (7) found that marls were the most reactive material for SO_2 capture.

CHEMICAL COMPOSITION OF SORBENTS

As only CaO reacts with SO_2, obviously the higher the content of that compound the greater will be the SO_2 capacity of the stone providing it has a porous structure to allow access of the SO_2 to the calcium. Greek marble, although over 99% $CaCO_3$, is not porous and has a low SO_2 capacity (4).

Some investigators have indicated higher sorbent capacities with higher Na content (3). This may be because Na can cause a more porous calcine, as will be discussed later. Iron as Fe_2O_3 or FeO(OH) also has been credited with a slight increase in reactivity (4, 5, 7). As pyrite, it reduces reactivity. Other impurities appear to exercise little influence on sulphation.

PARTICLE SIZE

The particle size of limestone added to the FBC has a considerable influence on the sorbent utilization. In practical applications the minimum particle size is largely determined by the air fluidizing velocity of the unit. The fluidizing velocity is in turn based on the unit size, energy output required, coal feed rate, etc. Within limits this also dictates the

particle size of the sorbent for if the particles are too fine they will be elutriated from the bed. Most AFBC units now being built operate in the 1-2½ m/sec range and use limestone passing 6300-2000 μm sieves. Limestone which is crushed to pass a specific sieve size e.g., 6300 μm (¼ in.) will, of course, include particles of all sizes down to dust. The size distribution will depend upon the hardness and grain size of that particular limestone. Unless the limestone is double screened to remove the fines, which is an additional expense, this fine material will be elutriated from the bed. It may be reinjected from the cyclone back to the bed for more efficient utilization of the sorbent.

Small particles have faster reaction rates and greater sulphation capacities than larger ones due to increased surface area and exposed pore volume (1,8). If the particle was sufficiently small it should sulphate completely. Borgwardt and Harvey (6) sulphated 11 types of limestones, each in three particle sizes; 1300 μm, 250 μm and 96 μm, and found that each type of stone had a different response of sorbent capacity to particle size. The limestone utilization, expressed as Ca/S, showed no difference between the largest and smallest particles for a lake marl. For a calcite sample, however, the Ca/S ratio varied by a factor of 10 over the range of particle sizes.

ATTRITION

Attrition is a term used to cover the loss or elutriation of material from the bed due to breakdown of sorbent particles. Decrepitation, thermal shock shattering, fragmentation during calcination and sulphation, abrasion of particles with each other and furnace internals all contribute to the loss of sorbent. The amount of attrition is dependent upon some, as yet poorly defined, properties of the sorbent and upon some operating parameters of the FBC (29). Argonne National Laboratories (ANL) investigated attrition with closely sized stones in both hot and cold fluid bed tests (9, 10). When raw stone was charged to a 900°C (5 cm dia) empty test bed and fluidized with gas containing SO_2 it was found that the greatest particle size decrease occured within the first ten minutes. With stones precalcined in a CO_2/N_2 fluidizing gas the attrition rate is high for the first 0.5 h and decreases to a steady state in about 1 h. The attrition rate increased

with increasing fluidizing velocity and also with increased bed depth. Both abrasion, and thermal shock contribute to attrition. Sulphation of a stone may decrease its attrition rate, presumably by the formation of a harder $CaSO_4$ surface layer as compared to attrition in calcination only tests. The $CaCO_3$ content does not appear to have an influence but greater quantities of impurities, Al, Si and Fe, may produce more resistant stones. Moisture within the stone may cause it to be a "popper", that is, to break up excessively. It appears almost impossible to predict a stone's resistance to attrition other than by testing and comparing the results to other stones.

TEMPERATURE

The temperature range used for FBC is 700-1000°C. Results of several investigators who studied sulphur removal over a range of temperatures indicate that the optimum temperature is in the range 760°C to 900°C. Hartman and Coughlin used the criteria of time of exposure to synthetic fluid gas to obtain a 17% conversion of calcium oxide to sulphate (11). The stones were not precalcined. The fastest sulphation reaction occurred at 900°C. Using thermogravimetric analysis (TGA) on stones calcined in 60% CO_2/N_2, O'Neill determined that maximum calcium sulphation occurs at 850°C and that efficiency declines on either size of the maximum (8). Data from the Babcock and Wilcox 6 x 6 ft. AFBC pilot facility confirmed O'Neill's work (40).

METHODS OF IMPROVING LIMESTONE EFFICIENCY

The techniques to improve limestone utilization can be divided into three categories: 1) pretreatment of the limestone prior to sulphation, 2) modifying the fluid bed parameters which affect sulphation, and 3) treatment of the sulphated stone to make it reuseable. Pretreatment includes precalcination in a CO_2 atmosphere, addition of a small quantity of salt or catalyst, and fine grinding and pelletizing with and without catalysts. The fluid bed operational parameters which significantly affect limestone efficiency are gas residence time, limestone particle size and temperature. Post sulphation treatment include grinding the sulphated stone and

pelletizing, and hydration of the sulphated stone. Most of these methods are reviewed in papers by Smyk (12) and by Newby et al (13).

PRE-SULPHATION TREATMENT

The most important characteristic of limestone relative to sulphation is porosity. When calcination is slow, such as with a high partial pressure of CO_2, fine pores consolidate into larger pores resulting in an increase in active area for sulphation. When calcination is rapid, as with a low CO_2 partial pressure or high temperature, e.g., 900°C, CO_2 is rapidly expelled leaving a fine pore structure. Westinghouse did considerable work on precalcination in a CO_2 atmosphere (15-60% CO_2) and have shown that the utilization of some limestones can be more than doubled (2). Other stones are affected to a lesser extent. Although precalcining limestone to porous lime would be a separate operation and hence more expensive, the improvement in efficiency may more than compensate for this (8).

The addition of a small quantity of salt to the limestone or with the limestone going into the combustor can significantly increase its efficiency of sulphur capture (15). The more common salts tested were CaCl, KCl, $CaCl_2$ and Na_2CO_3. When salt-treated limestones are exposed to fluid bed temperatures above 700°C, trace amounts of liquid form which increase the mobility of ions in the CaO matrix. The higher mobility via surficial liquid films enhances crystallization of CaO and $CaSO_4$. Large pores form at the expense of small pores thereby increasing limestone reactivity. Argonne National Laboratory has published many reports on their work with his method (16-19). They reported decreases in limestone requirements of up to 50% with salt addition to some stones. Unfortunately the addition of these alkali salts, the more effective ones being chlorides, can cause accelerated corrosion of the boiler tubes in the fluid bed combustor. It is claimed that the addition of approximately 2 mol % Na_2CO_3 or $CaCl_2$ does not cause additional corrosion (16). The costs of salt addition would be very small compared with the potential saving in limestone usage.

A small quantity of Fe_2O_3, added either as powder or as an aqueous solution of ferric sulphate, has been reported by Yang to have a significant beneficial effect on limestone utilization (20, 21). The Fe_2O_3 is capable of catalysing the sulphation reaction, that is, oxidizing SO_2 to SO_3. The Fe_2O_3 also increases the capacity of limestone for SO_2 absorption although

the reason for this is not known. Tests on Greer limestone indicated Fe_2O_3 can almost double the limestone utilization. On the other hand Burdett (22) claims that the forced oxidation of SO_2 to SO_3 by iron oxide decreases the overall sulphation capacity by exerting diffusional barriers of $CaSO_4$ at a faster rate than normal conditions. However, the iron content of this test stone was increased from 0.2% to only 0.3% which may not have had the same positive effect as the up to 4% Fe_2O_3 used by Yang.

As previously discussed, very fine particles, because of the greatly increased surface area of the limestone and hence greater overall exposed porosity per mass, have a greater SO_2 capture efficiency than do large particles. However, fine particles of limestone added to the combustor are almost immediately elutriated from the bed by the fluidizing air. Agglomerating the particles by pelletizing may provide the benefits of fine particles without this disadvantage. Some work has been done with pelletizing regenerable sorbents such as portland cement (23) and also on agglomeration of coal ash and sulphated limestone (24). Although this latter paper suggests pelletizing raw limestone, no experimental work was reported. Pelletizing limestone forms part of this planned investigation and will include blending of catalysts into the pellets. It will be covered in the next report.

FLUIDIZED BED OPERATING PARAMETERS

The conditions under which the fluid bed combustor operates have a significant effect on the utilization of the sorbent and on SO_2 retention. The principal parameters affecting SO_2 capture are temperature, gas residence time and feed particle size. Unfortunately the optimum conditions for thermal efficiency do not completely coincide with those for SO_2 capture efficiency. The maximum reactivity of limestone occurs about 850°C and tapers off gradually on either side. Optimum combustion efficiency occurs with bed temperature of 900° to 950°C.

Gas residence time, which is defined as the expanded bed height divided by superficial gas velocity, can vary from less than a second up to two or three seconds. With short gas residence times there is less time for SO_2 molecules to be captured by limestone, so that increased residence time results in greater SO_2 retention. Thus SO_2 emission specifications can be met by a low gas velocity and a shallow bed or a higher velocity and a deep

bed. Although achieving a sufficient gas residence time is necessary to bring the SO_2 concentration in the off-gas to within emission limits, it does not affect the overall utilization of limestone, as the solids residence time is several hours or more. It does mean that a more reactive limestone will permit the use of a shallower bed or higher gas flow than a less reactive limestone.

Particle size effect has already been discussed. It is perhaps the most influential parameter in the overall combustor performance (25). Although more effective for SO_2 capture, fine particles are elutriated from the bed. Techniques such as recirculating cyclone fines back to the bed can be used to improve overall limestone utilization.

POST-SULPHATION TREATMENT

Sorbents leaving the combustor have a shell of $CaSO_4$ and an unreacted core of CaO. The calcium sulphate formed has effectively blocked off the surface and the pores thus retarding further sulphation. This material can be reactivated by grinding and agglomeration, or by hydration. A third possibility is regeneration whereby $CaSO_4$ is decomposed to CaO and SO_2 at temperatures of 1100°C. The liberated SO_2 must then be treated by a further process to produce sulphur, acid or sludge. The complexity and cost of this approach excludes it from further consideration.

Grinding and pelletizing spent bed material and cyclone dust can greatly improve the efficiency of limestone usage as well as combustion efficiency (24). Grinding exposes unreacted lime and blending in cyclone dust with incompletely reacted fine particles, both lime and carbon, and pelletizing permits all this material to be recycled for further sulphation. This material reportedly acts as its own binder when mixed with water. Pellets would be made a different size from the spent bed material so that the sulphated pellets could be removed by screening. In an assessment by R.A. Newby et al, of advanced processes for improving the utilization of sorbents, this method was recommended as being the most attractive option for further development work (13).

The hydration of partially sulphated sorbent to reactivate it for further sulphation has been the subject of a number of reports by Argonne (26, 27). Upon exposure of sulphated lime to water or low temperature steam, water diffuses through the sulphated shell and hydrates some CaO to

$Ca(OH)_2$. Because the molar volume of the hydroxide is greater than the oxide, its formation causes cracks to open in the sulphate shell. When the hydrated sorbent is returned to the combustor the $Ca(OH)_2$ dehydrates to CaO which shrinks and opens up a new pore structure within the lime core; thus more material is available for sulphation. This process may increase the limestone utilization by greater than a factor of two. It appears that poor limestones generally benefit more from this treatment than good stones. The process may be repeated several times until the limestone is essentially completely sulphated. For most efficient utilization of the process Argonne National Laboratory proposed a plug flow mode with three AFBC's and hydrators in series. Such a system would reduce the quantity of sorbent required by a reported 61% (15). An alternative approach, although not as efficient but certainly less expensive, would be to use a two compartment combustor.

LIMESTONE SAMPLES

The limestones for this project were supplied by J.H. Fowler, Geologist, Nova Scotia Department of Mines and Energy, D.E. Barnett, Geologist, New Brunswick Department of Natural Resources, N.D. O'Donnell, Section Head, Geology, Syncrude Canada Ltd., and C.F. Lamb, Senior Geologist, Canstar Oil Sands Ltd. Sample quantity was 20-40 kg. Table 1 gives the descriptions of the locations of the samples. An additional four Nova Scotia samples were later obtained from locations previously sampled. In total, five of the Nova Scotia samples and all of the New Brunswick samples came from operating quarries. The samples for Brookfield, Nova Scotia arrived in separate drums and were treated as separate samples. The sample from Gays River, Nova Scotia is dolomite tailings from a lead-zinc mine and was included to see if this material could be pelletized and used as an SO_2 sorbent. Unfortunately this mine has since closed. All the remaining samples come from undeveloped deposits.

Samples representative of the crushed stone were taken for petrographic and chemical analysis. Chemical analyses are given in Table 2. As part of this and another project, most Nova Scotia stones were analysed for as many trace elements as possible by optical spectroscopy. These results are given as Table 3.

At a later date, September 1982, the author collected a number of samples at Havelock Lime Works, Havelock, N.B. This company supplies limestone for the fluidized bed unit at Canadian Forces Base, Summerside, P.E.I. This company obtains its limestone from two quarries; their own at Samphill and also from Canada Cement Lafarge's at Havelock. Both quarries are in the same geological formation although are about 9 km apart. Samples were taken from various locations at the Havelock operation. In addition samples were available from several shipments since 1980 to the Combustion and Carbonization Research Laboratory. Because Samphill limestone is reddish and Canada Cement's is grey, the source of the earlier samples could be defined. Finally two samples were obtained from the first two truckload shipments delivered to CFB Summerside. Thus 9 samples representing production from one limestone plant operating on two quarries over approximately a two year period were available for testing. Table 4 gives the chemical analyses of the composite samples.

Table 1 - Origin of limestone samples

	Nova Scotia
GR-1	Canada Wide Mines Ltd., Gays River, Halifax County. Sample of dolomite fines from the mine tailings pond.
NS-1 NS-9	Limestone samples from the Scotia Limestone quarry at Irish Cove, Cape Breton County.
NS-2	Dolomite sample from the Scotia Limestone deposit at Kelley Cove, Victoria County.
NS-3	Dolomite sample from Mosher Limestone Co. Ltd. quarry at Upper Musquodoboit, Halifax County.
NS-13	Limestone sample from Mosher Limestone Co. Ltd.
NS-4 NS-8	Limestone sample from the Canada Cement Lafarge Co. Ltd. quarry at Brookfield, Colchester County.
NS-5 NS-10	Limestone sample from Havelock Lime Works quarry at Southside Antigonish Harbour, Antigonish County. Known as Calpo Limestone.
NS-6	Metallurgical and cement grade limestone from a large deposit at Glencoe, Inverness County, owned by Scotia Limestone.
NS-7	Dolomite from the same deposit as NS-6.
NS-11	Composite sample from 31'-290' section of dill core D-8 Glencoe deposit.
NS-12	Composite sample from 9'-230' section of dill core J-2 Glencoe deposit.

New Brunswick

NB-1	Limestone sample from Havelock Lime Works, Samphill quarry at Havelock. Sample taken from a 10 t shipment to Combustion and Carbonization Research Laboratories (CCRL) 1980.
NB-1-3	Limestone sample from CCRL, Canada Cement material from screened 8 x 20 M sample, March 1982.
NB-1-4	Limestone "-¼ inch" from Samphill waste pile
NB-1-5	Limestone "-¼ inch" from Canada Cement waste pile
NB-1-6	Limestone hand picked from Samphill quarry face
NB-1-7	Limestone "-3 x 1¼ inch" from Samphill pile
NB-1-8	Limestone "-½ x ¼ inch" from Canada Cement pile
NB-1-9	Limestone "-¼ inch" truckload of Samphill to CFB Sunniside
NB-1-10	Limestone "-¼ inch" truckload of Canada Cement to CFB Sunniside
NB-2	Limestone sample from quarry at Carlisle, Carleton County.
NB-3	Dolomite sample from Brookville Manufacturing Co. Ltd., quarry Brookville, Kings County.
NB-4	Limestone sample from the Elm Tree quarry, near Petit Rocher, Gloucester County.
NB-5	Limestone sample from the Windsor quarry, Carleton County.

Alberta

CS-1	Limestone sample from outcrop at Clausen's Landing on the Athabasca River.
SY-1	Limestone sample from outcrop on Syncrude Canada Ltd. property adjacent to Provincial Highway 963.
SY-2	Limestone sample taken during the quarrying of 50 t in March, 1983, same location as SY-1.

Table 2 - Chemical composition of sorbents (m %)

Sample		$CaCO_3$	$MgCO_3$	Fe_2O_3	Al_2O_3	SiO_2	Na_2O	K_2O	S
Nova Scotia									
GR-1	Gays River tailings	54.4	32.6	1.36	1.37	7.14	0.23	0.24	0.03
NS-1	Irish Cove	94.4	1.0	0.31	0.32	1.20	0.03	0.04	0.02
2	Kelly Cove	52.4	42.2	0.49	0.33	6.17	0.01	0.02	0.01
3	Upper Musquodobit	50.6	40.4	0.94	0.98	6.38	0.16	0.12	0.02
4	Brookfield	83.9	1.97	1.32	3.13	12.3	0.08	0.83	0.15
5	Calpo	95.6	1.99	0.21	0.22	0.99	0.07	0.05	0.03
6	Glencoe	86.7	10.1	0.49	0.83	3.27	0.04	0.17	0.03
7	Glencoe	93.9	3.87	0.21	0.42	1.28	0.06	0.06	0.02
8	Brookfield	86.3	1.0	0.87	2.63	8.33	0.06	0.66	0.08
9	Irish Cove	94.4	1.53	0.59	0.42	2.43	0.03	0.04	0.12
10	Calpo	96.1	0.90	0.27	0.13	1.49	0.02	0.02	0.11
11	Glencoe	92.1	3.84	0.44	0.59	2.15	0.01	0.17	0.08
12	Glencoe	92.4	4.52	0.30	0.40	1.68	0.01	0.10	0.04
13	Upper Musquodobit	92.8	0.32	-	-	-	-	-	-
New Brunswick									
NB-1	Havelock	94.6	1.83	0.37	1.37	3.08	0.03	0.15	0.02
2	Carlisle	98.4	1.0	0.21	0.45	0.71	0.04	0.03	0.02
3	Brockville	54.1	45.0	0.23	0.57	1.54	0.04	0.09	0.01
4	Elm Tree	91.5	1.0	0.57	1.53	7.02	0.04	0.23	0.01
5	Windsor	97.6	1.63	0.13	0.14	0.32	1.31	0.07	0.01
Alberta									
CS-1	Canstar	90.1	2.89	0.83	2.04	8.32	0.06	0.54	0.01
SY-1	Syncrude	91.3	2.49	1.00	1.34	5.98	0.03	0.23	0.10
SY-2	Syncrude	75.6	2.50	1.59	3.93	14.35	0.04	0.93	-

Table 3 - Optical emission spectroscopic analysis

Element	Min. detection Limit m %	NS-1	NS-2	NS-3	NS-4	NS-5	NS-6	NS-7
Ti	0.0003	.015	.005	.02	.07	.01	.03	.01
Mn	0.0001	.7	.05	1	.02	.5	.01	.005
Ag	0.0003	-*	-	.0003	-	-	-	-
B	0.0015	-	-	.002	.005	-	.002	.0015
Ba	0.0003	.03	.0015	.005	.015	.02	.015	.002
Be	0.0001	-	-	-	.0001	.0002	-	.0001
Co	0.0001	.001	.001	.001	.001	.001	.001	.001
Cr	0.0007	-	.03	.0007	.005	.0007	.002	.0015
Cu	0.0002	.0007	.001	.0007	.005	.0007	.002	.001
Ge	0.002	-	-	.003	-	-	-	-
Mo	0.002	.003	.003	.002	.002	.002	.002	.002
Nb	0.002	.003	.003	.003	-	.002	.003	.003
Ni	0.001	.003	.007	.002	.01	.002	.002	.002
Pb	0.007	.01	.02	-	-	-	.02	-
Sc	0.0003	-	-	-	.0007	-	.0003	-
Sn	0.003	-	-	-	-	-	.003	-
Sr	0.0003	.02	.003	.005	.03	.03	.02	.01
V	0.001	-	.001	-	.002	-	-	-
Y	0.001	.001	.001	.002	.002	.005	.002	.001
Zn	0.02	.05	.02	-	.02	.02	-	-
Zr	0.001	.001	-	.003	.005	.001	.002	.001

The following elements were analysed but not detected at the minimum detection limits:

P 0.07, As 0.03, Au 0.007, Bi 0.007, Cd 0.007, Ce 0.003, Hf 0.005, La 0.003, Nd 0.005, Sb 0.02, Ta 0.2, Te 0.2, Th 0.01, U 0.015, W 0.007, Yb 0.0002, In 0.002, Pd 0.007, Pt 0.005, Tl 0.03

* - less than detection limit

Table 4 - Chemical analysis - Havelock limestone

Sample No.	Description	$CaCO_3$	$MgCo_3$	Fe_2O_3	SiO_2	LOI	Total
NB -1-1	Samphill from CCRL	94.60	1.83	0.37	3.08	41.61	99.88
1-3	Canada Cement, CCRL 8 x 20	98.41	1.37	0.20	1.44	42.68	100.42
1-4	Samphill waste pile	83.08	1.62	1.16	11.42	36.52	97.28
1-5	Canada Cement waste pile	94.08	1.32	0.59	4.87	40.34	100.86
1-6	Samphill quarry face	100.43	0.63	0.16	1.48	42.80	102.70
1-7	Samphill 3 x 1½ inch	101.00	0.59	0.17	1.11	42.96	102.87
1-8	Canada Cement ¾ x ¾	99.06	1.11	0.19	1.62	42.76	101.98
1-9	Samphill 1st truck load to CFB S'side	92.13	0.0	0.44	3.22	42.01	99.07
1-10	Samphill 2nd truck load to CFB S'side	92.71	0.0	0.36	3.02	42.59	99.66

Note: Sample 1-4 appears very low, probably not representative
Second analyses on -841 + 250 µm 97.35% $CaCO_3$

PETROGRAPHIC STUDY OF LIMESTONES

Thin sections were made of particles of three limestone samples, NS-1 Irish Cove, NS-10 Calpo, and NS-12 Glencoe. Photomicrographs of the stones are given as Figures 1, 2, and 3. The calcium component has been stained with alizarin red 5 dye; this dye does not affect dolomite.

Irish Cove limestone is a fine grain fossiliferous calcite. Occasional particles show grains of dolomite. Calpo is also a fine grain fossiliferrous calcite. Many particles exhibited macroporosity. The Glencoe sample exhibited variable grain size up to fairly massive crystals. It is a recrystallized limestone interspersed with dolomite. Some particles were black and contained visible pyrite crystals. A few of these particles were examined by X-ray diffraction which indicated the presence of chlorite, pyrite, quartz and mica. Therefore, although in the chemical analyses the magnesium is expressed as carbonate, some of it is actually a magnesia-silicate hydrate.

Fig. 1 - Irish Cove, NS-1 limestone, 30x

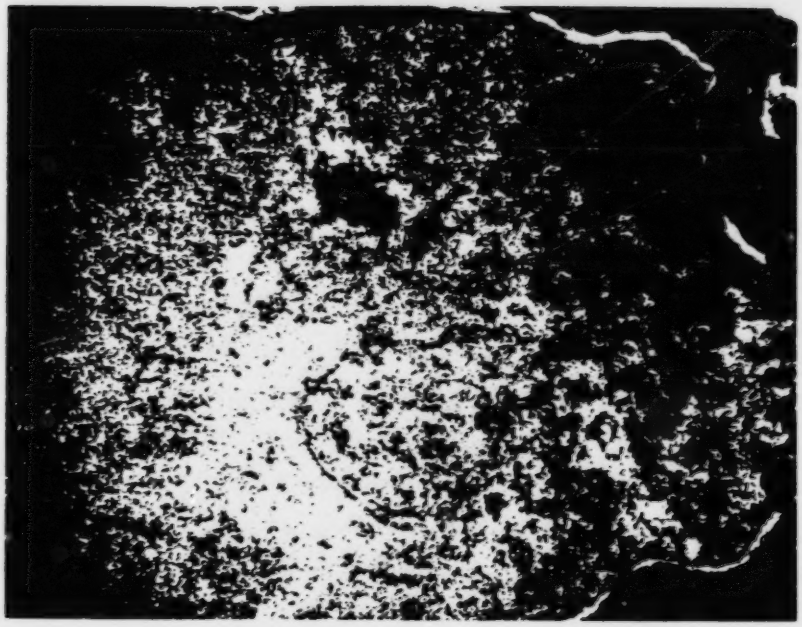

Fig. 2 - Calpo, NS-10, limestone, 30x

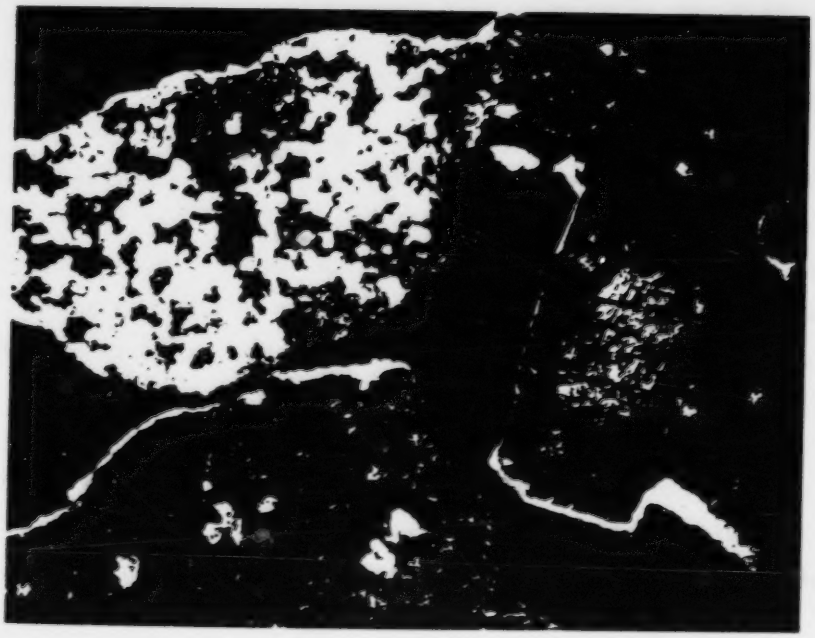

Fig. 3 - Glencoe, NS-12, limestone, 30x

EXPERIMENTAL APPARATUS AND PROCEDURE

FLUIDIZED BED TEST REACTOR

A bench scale fluidized bed reactor was designed and built for testing the SO_2 capture capacity of limestones, a schematic of which is shown as Fig. 4. The reactor is 53 mm i.d., (2 inch, schedule 40 pipe) 316 stainless steel, flanged at both ends with flat top and bottom plates. 316 stainless steel was used because it was readily available although 310 stainless steel would have been the preferred material. The reactor height of 1.45 m is made up of two pipes joined with flanges 0.35 m from the bottom. The internal diameter of the bottom center flange was machined to accept a 60 mm diameter by 4.6 mm thick porous silica disc, 40-90 μ porosity, which is used as the distributor. The pipe below the distribution is filled with ceramic saddles and is used as a preheater. Four pairs of half cylindrical resistance heaters each with their own thermocouple and powerstat are used to provide uniform heating to the reactor. Proportional controllers are scheduled to be installed on these heaters. Additionally heater tape is wrapped around the incoming gas line. Bed temperature is monitored with a thermocoumple approximately 30 mm above the distributor. With a 250 g sand bed the heat up time to 850°C is less than 2 hours.

Initially synthetic flue gas to the reactor was made up by metering through rotameter the respective quantities of CO_2, O_2, SO_2 and N_2. An electronic mass flow controller was then installed on the SO_2 gas line and an electronic mass flowmeter installed to measure the total gas volume into the reactor. A Beckman model 865 infrared analyser with a chart recorder is used for continuous SO_2 analysis. The gas composition can be analysed before and after the reactor. Manometers measure the gas pressure to the reactor and the differential pressure across the reactor.

Material is added to the reactor from a hopper. It is removed from the reactor with a vacuum system which collects the sample via a tube whose open end is 3 mm above the distributor. The system removes all but 2 or 3 g from the reactor. Dust from the reactor is collected by a cyclone on the exhaust line.

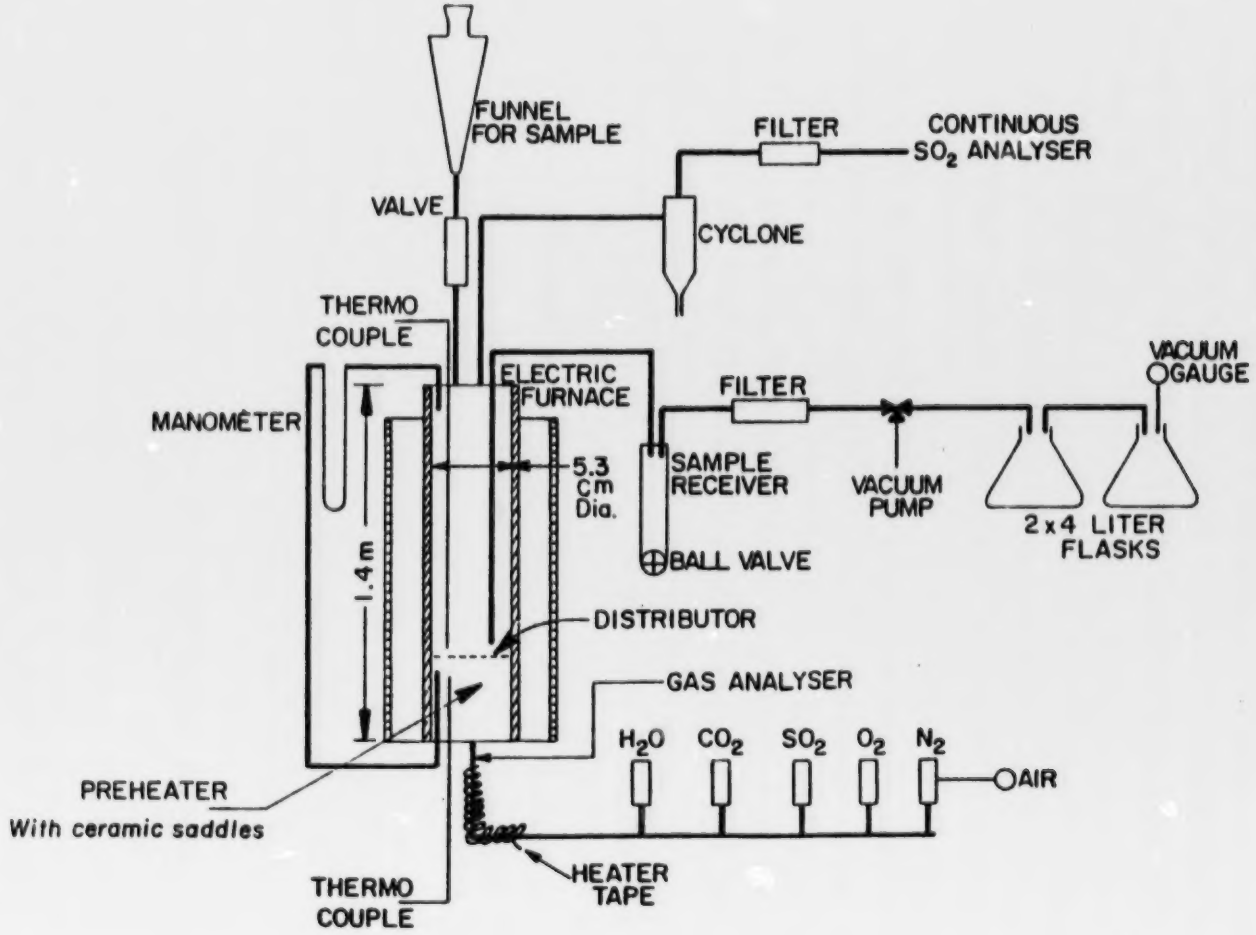

Fig. 4. Bench scale fluidized bed reactor.

The reactor was characterized with graded Ottawa pure silica sand, ASTM C-109, average particle size 400 μm. The minimum fluidizing velocity, U_{mf}, was determined as 20 cm/sec. with a bed of 250 g sand at 22°C. From literature data (28) on the influence of temperature on U_{mf}, U_{mf} at 850°C should be approximately 10 cm/sec. The reactor was normally operated at a fluidizing velocity, U_0, of 52 cm/sec. at 850°C, i.e., about 5 times U_{mf}. Most sulphation tests were conducted with a bed of 250 g sand and 10 to 50 g limestone which gave a gas retention time of 0.55 to 0.60 s. Gas retention time is defined as expanded bed height divided by superficial gas velocity. The expanded bed height was 30 cm.

For each test the furnace was heated to 850°C with a bed of 250 g sand and air as the fluidizing medium. The air was then turned off and synthetic flue gas, admitted to the system (0.25-0.50% SO, 8% CO_2, 5% O_2 with the balance nitrogen). This composition could be changed as desired. After reaching 860°C the dry, screened and washed limestone sample was injected into the reactor. The temperature dropped by 10 to 20°C depending on the sample mass but recovered to 850°C within 10 minutes. The SO_2 in the exhaust gas was continuously analysed and graphed on a chart recorder. Several times during each run the Beckman analyser was switched to an analysed SO_2/N_2 bottled gas to check instrument calibration. It was also switched to check that in-coming synthetic gas to the reactor remained constant. At the conclusion of a test run, normally 2-4 h, all the bed material was withdrawn by vacuum into the sample receiver. The sample was weighed and portions of it were submitted for chemical analysis. The cyclone dust was also weighed and analysed.

CONTRACT WORK - ASSESSMENT OF LIMESTONE FOR FLUIDIZED-BED COMBUSTION

Two contracts, one by Nova Scotia Power Corporation, NSPC, for the assessment of four stones and a second by CANMET for the assessment of up to 20 stones, were let to Dr. Irving Johnson, Clarendon Hills, Illinois (41). The contract entailed thermogravametric analyses (TGA) of the stones, predicting the Ca/S feed ratio versus sulphur retention using the Argonne National Laboratory model applied to fluid bed combustors, determination of stone decrepitation, and comparison with results of other stones which have been used in large scale fluid bed combustors. The NSPC contract covered

the assessments of limestones: NS-9 Irish Cove, NS-10 Calpo, NS-11 and 12 Glencoe. The model was applied to the proposed NSPC 1 m^2, 10 000 h corrosion test rig to be built at Port Hawkesbury, Nova Scotia. The CANMET contract covered the remainder of the sample stones plus some modified limestones. In the latter contract the model was applied to the Summerside FBC and CCRL's test rig (30).

In the TGA work 0.3 to 0.4 g of -1.00 mm + 850 µm stone was first calcined to 850°C in 20% CO_2, balance N_2 until a constant weight was obtained and then sulphated in 0.3% SO_2 during which the weight gain due to sulphation was recorded with time.

RESULTS AND DISCUSSION

Typical graphs of the SO_2 concentration in the exit gas from the fluidized bed reactor is given as Fig. 5 which represents a test series wherein 10 g of 841-1000 µm sorbent was exposed to 0.28% SO_2 flue gas at 850°C. Within a minute of adding the limestone the SO_2 concentration in the exit gas drops to a fraction of the inlet concentration. It then begins to increase, the rate of increase being dependant upon each particular limestone. After one to four hours, depending upon the limestone and the mass of sample, the exit SO_2 concentration stabilizes at or very near to the inlet concentration.

The area above the curve on the graph up to the value of the inlet concentration is proportional to the quantity of SO_2 captured by the sorbent. The sulphation capacity of the sorbent can therefore be calculated by:

$$X\% = \text{sulphation} = \frac{\text{area } SO_2 \text{ captured} * \text{mol } SO_2/\text{min} * t(\text{min})}{\text{area } SO_2 \text{ input} \quad * \text{mol Ca}}$$

A sulphation curve is generated by a computer program which applies Simpson's Rule to the emission curve. A reiterative non-linear least squares regression program is used to fit the sulphation points to an empirical equation and to draw a curve best fitting the equation:

$$X\% = a(1-\exp(-kt^n))$$

These curves, Fig. 6-9, make it possible to compare sorbents for SO_2 in a fluidized bed providing that the same conditions are used for each test. The parameter "a" closely approximates the maximum sulphation capacity "X". It is independant of the quantity of sample and the SO_2 concentration. It is, however, dependant upon the particle size as sulphation capacity generally increases with decreasing size. The parameters "k" and "n" vary with all three. Similar curves fitting the same equation result from thermogravimetric analysis of sorbents. It is possible, providing that the sulphation capacity of a sorbent is approximately the same value in both the TGA and the fluidized bed reactor, to obtain the same or almost equal values for "a", "k" and "n" from both test methods. In this case the same particle size, 841-1000 μm, is used in both tests, and the fluidized bed reactor operates with 10 g sample. The SO_2 feed rate is 0.0021 moles/min which produces a synthetic flue gas of approximately 2750 ppm compared to 3000 ppm used in the TGA. The parameters "a", "k" and "n" are used in modelling which will be discussed in a later section of the report.

The sulphation capacity is also attainable from the chemical analysis of calcium and sulphur in the sulphated bed and cyclone material. In order to improve the accuracy of the analysis the sulphated limestone was separated from the silica sand which formed the bulk of the bed material. With fine limestone feed, 212-841 μm, a heavy liquid separation technique was attempted. The efficiency of the separation was very much dependant upon the particular sorbent. Its density was dependant upon the raw particle density and upon the particle size. The finer the particle size, the greater the degree of sulphation and consequently the higher the density. In many cases the density of the sulphated stone spanned that of the silica, 2.65-2.70 g/cc, so that a clean separation was not possible.

In the case of limestone in the 841-1000 μm size reasonably good separation was achieveable by simple sieving with a 595 μm screen. Only a few percent of the silica was coarser than this and a few percent of the sulphated stone, finer.

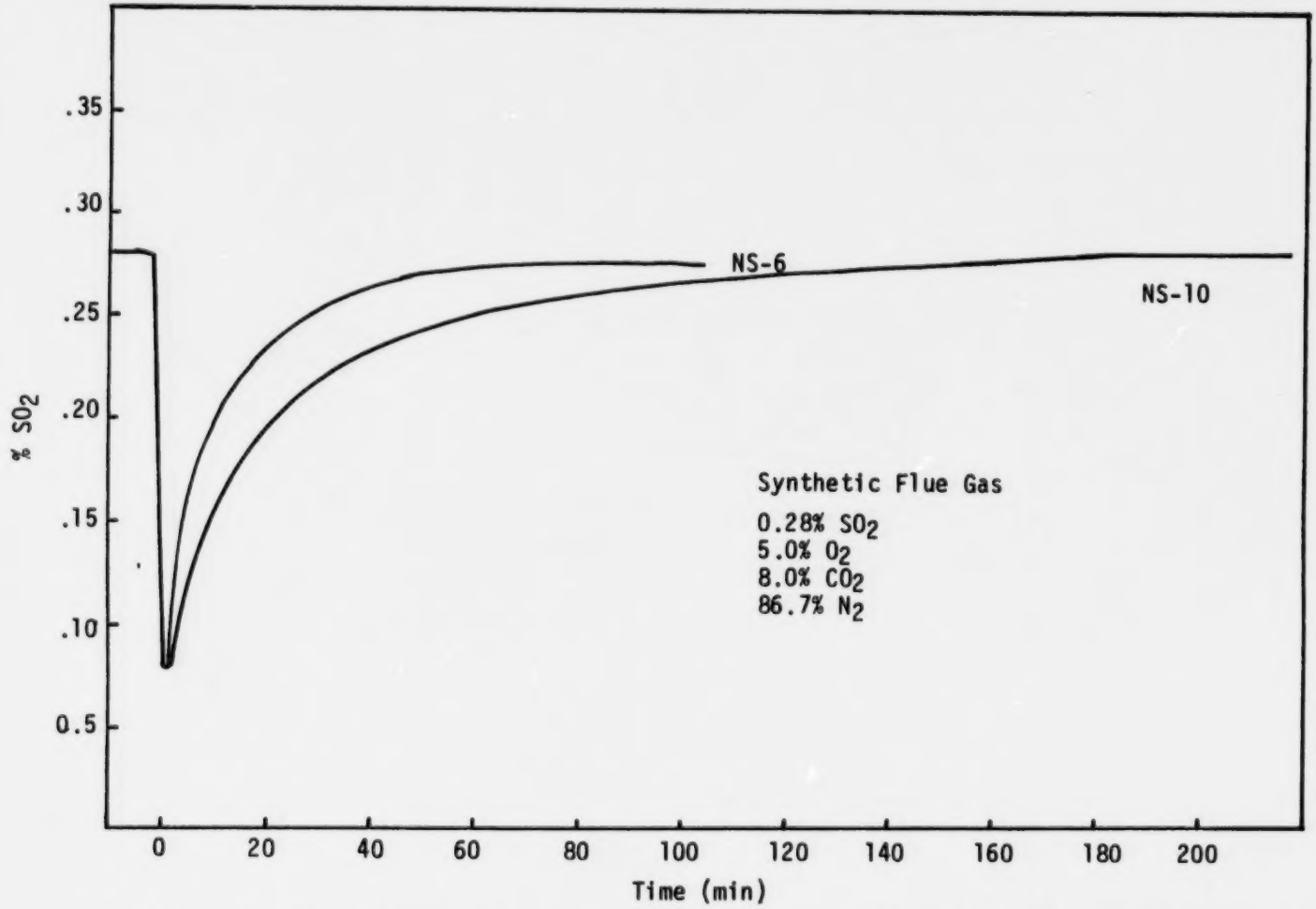

Fig. 5. SO_2 concentration in exit gas after adding 10 g, 841-1000 μm sorbent, 850°C.

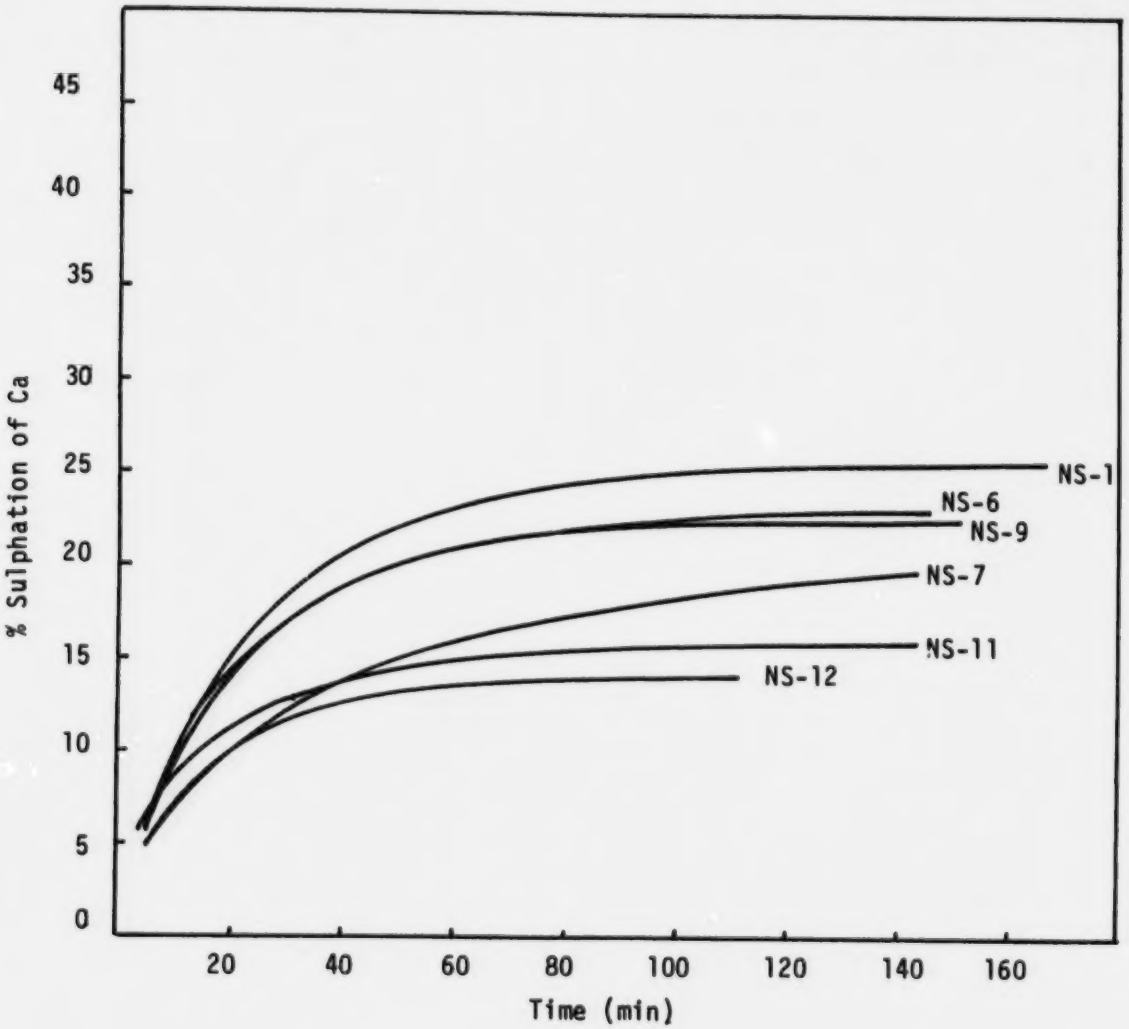

Fig. 6. Sulphation curves of Nova Scotia sorbents, 0.3% SO_2 850^{o}C, 841-1000 µm

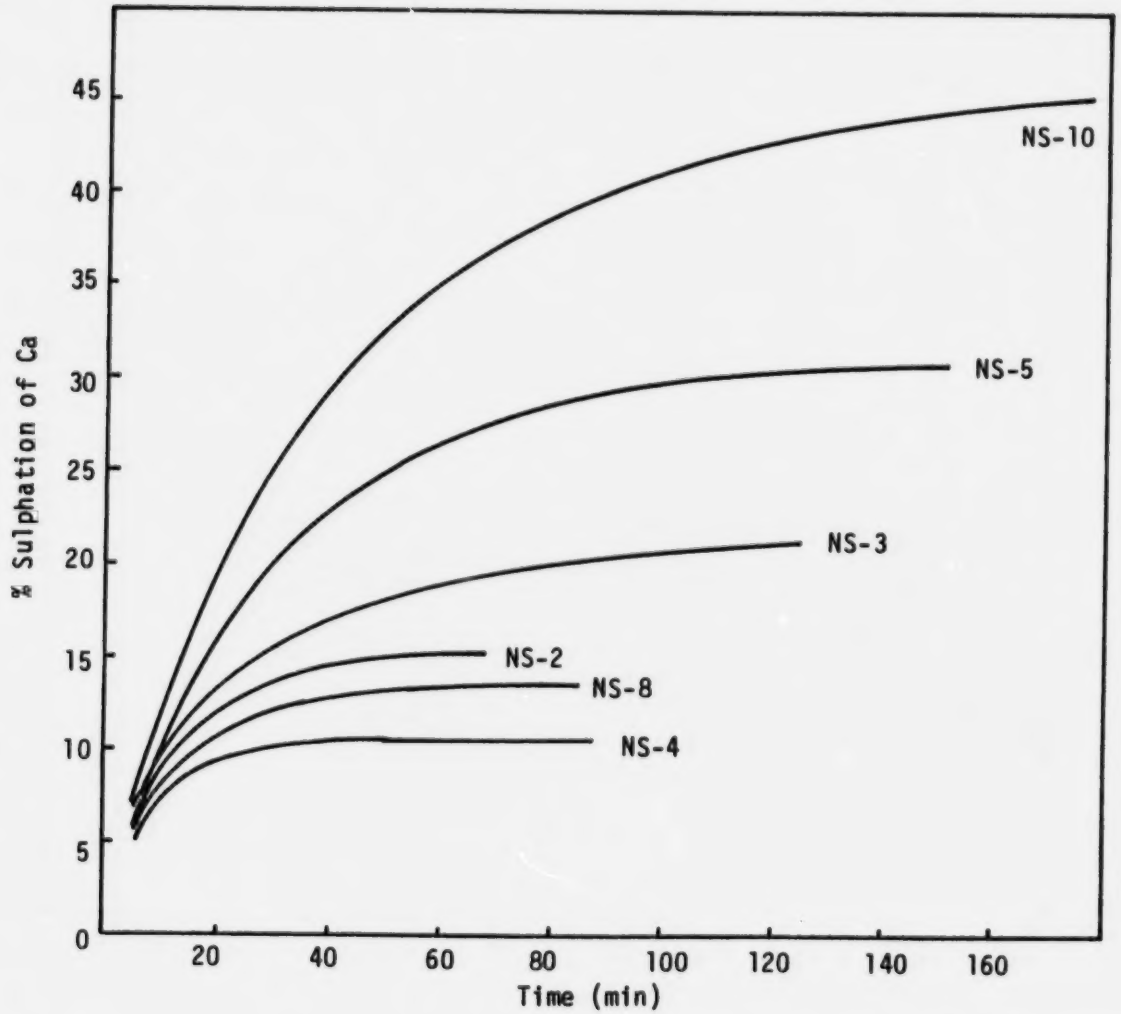

Fig. 7. Sulphation curves of Nova Scotia sorbents, 0.3% SO_2 850°C, 841-1000 µm

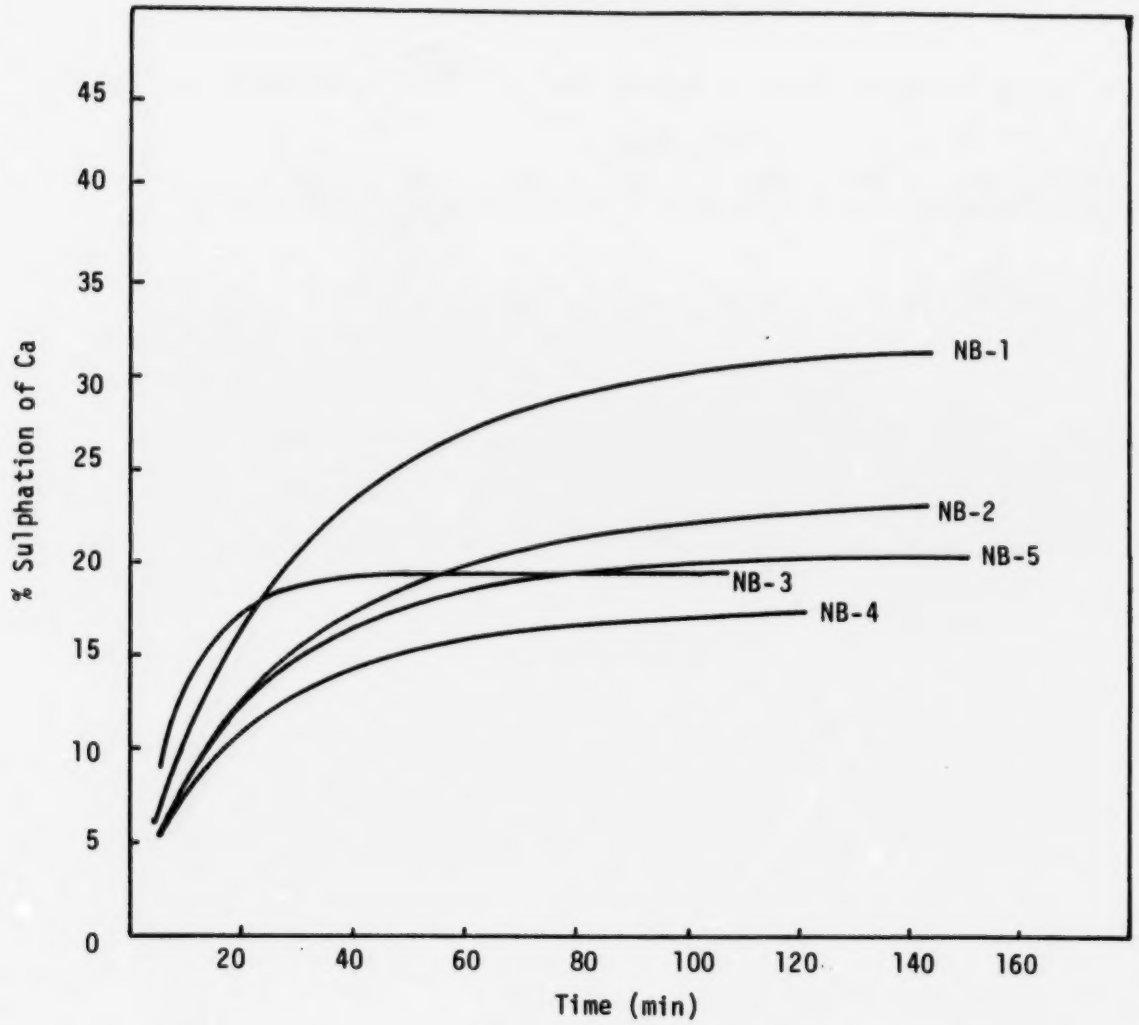

Fig. 8. Sulphation curves of New Brunswick sorbents, 0.3% SO_2 850°C, 841-1000 μm

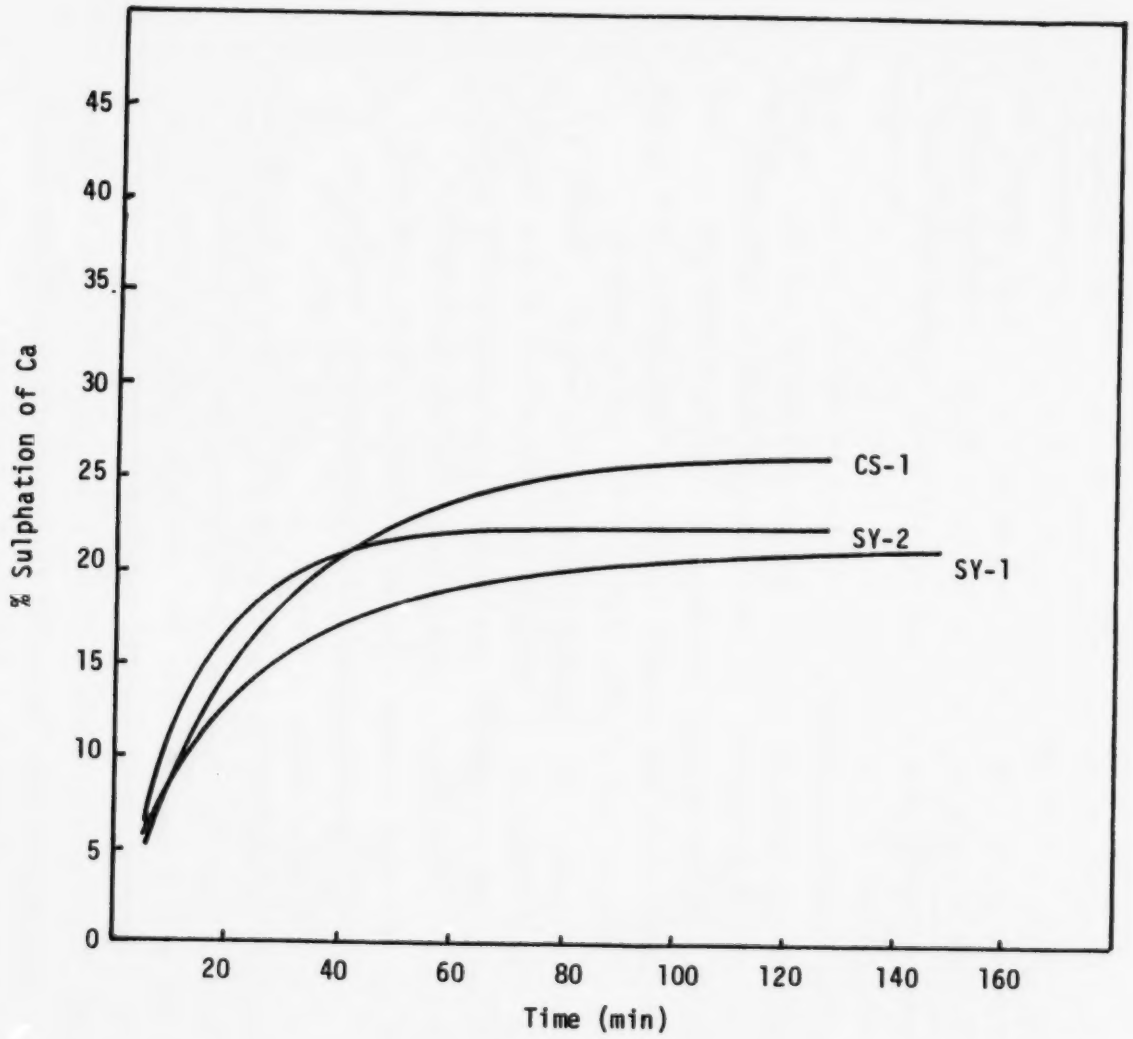

Fig. 9. Sulphation curves of Alberta sorbents, 0.3% SO_2, 850°C, 841-1000 μm

Fluidized Bed Reactor Sulphation Results

Twenty nine limestone and dolomite samples were tested in the fluidized bed test rig for reactivity with SO_2 in synthetic flue gas at 850°C. Most were tested in at least two different size ranges. With the same size material there is a large variation in SO_2 reactivity of the stones and in the extent of conversion of calcium carbonate to calcium sulphate. With limestone samples in the particle size 841-1000 μm the sulphation capacity varied from 10 to 46%. The sulphation curves for those tests are given in Fig. 6 to 9.

The sulphation curves of the two Irish Cove, NS-1 and -9, and the four Glencoe samples, NS-6, -7, -11 and -12, are shown in Fig. 6. Irish Cove is the better limestone and although the two samples were taken eight months apart, their results are similar. The two surface samples of Glencoe, NS-6 and -7, are somewhat better than NS-11 and -12 which are composites of about 100 m of two drill cores.

The remaining Nova Scotia limestones are given in Fig. 7. Calpo limestone, NS-5 and -10, have the best sulphation capacity of all the sorbents tested. There is however, a considerable difference, 31.8 verses 46.1%, between the two samples eight months apart. Kelly's Cove and Musquodobit, NS-2 and -3 are both dolomites. The former exhibits very little sulphation capacity, about 11%. Part of this low capacity is attributable to the thermal shock decrepitation of this sorbent. Within a few minutes of adding the stone to the reactor 20-30% of the initial sample mass is collected in the cyclone receiver. NS-3 is much better with a 21% conversion of the available calcium to sulphate. The two Brookfield samples, NS-4 and -8, which although they were collected at the same time, were shipped in different containers and hence considered as two samples, have very poor sulphation capacity at 10-12%.

The sulphation curves for the New Brunswick and the Alberta sorbents are plotted in Fig. 8 and 9. Havelock, NB-1, is the best New Brunswick stone with a 30% sulphation capacity. The remainder; Carlisle, NB-2, Windsor, NB-5, Brookville, NB-3, and Elm Tree, NB-4, have capacities ranging from 23 to 17%. The Alberta stones, Clarsion's Landing, CS-1, and Syncrude, SY-1 and 2, sulphated from 20 to 26%. The first two are surface samples and the latter is representative of 50 t quarried for FBC tests.

In the case of the Havelock deposit nine samples were collected representing a two year time period and two separate quarries within the

same geological deposit. The sulphation curves of six of these samples are given in Fig. 10. Although there is some variation in the capacity of the samples no significant difference was determined between the two quarries. It was concluded that limestone from either quarry would be acceptable for the Summerside FBC unit.

The sulphation capacity of all of sorbents are given in Table 5. Column 1 are the results of the 841-1000 µm sized particle tests whose curves are discussed above.

Table 5 - Sorbent sulphation capacity

Sample		FB Reactor % X 841-1000 µm	FB Reactor % X 297-595 µm	TGA % X 850-1000 µm	Chem. Analysis % X Bed 841-1000 µm
NS-1	Irish Cove	25.5		20.5	30.7
9		22.4	24.7	24.8	30.8
2	Kelly Cove	11.4	13.5	22.4	
3	Musquodobit	21.1	25.9	25.7	
4	Brookfield	10.5	13.9	16.7	
8		12.2		19.8	
5	Calpo	31.8		33.8	
10		46.2	41.9	42.1	45.9
6	Glencoe	21.3	29.8	25.5	23.8
7		20.5	20.4	24.9	20.9
11		16.2		26.3	20.7
12		14.8	15.2	23.6	19.9
13		24.8			
NB-1	Havelock	30.6	27.9	29.0	
1-3		25.4			
1-4		31.1			
1-5		27.2			
1-6		26.3			
1-7		25.4			
1-8		29.2			
2	Carlisle	23.0	21.8	20.8	25.1
3	Brookville	19.5	18.5	31.4	27.6
4	Elm Tree	17.2	20.5	14.2	
5	Windsor	20.3	24.1	17.7	
CS-1	Clarson's Landing	25.7	27.1	21.8	
SY-1	Syncrudes	20.6	32.0	19.3	25.1
2		22.3			

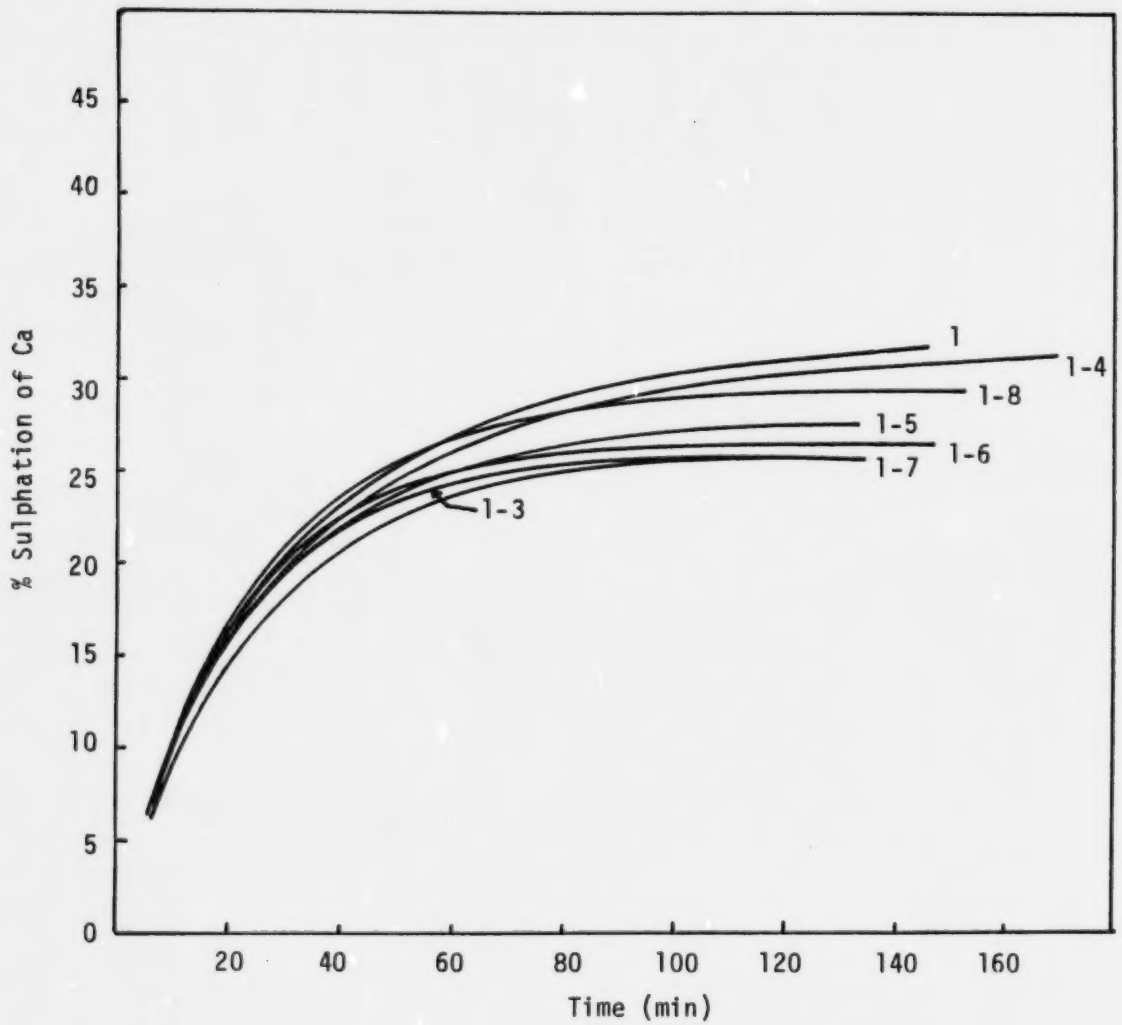

Fig. 10. Sulphation curves of Havelock, New Brunswick, limestones, 0.3% SO_2, 850°C, 841-1000 μm

PARTICLE SIZE EFFECT

At least one sample from each deposit was tested in the particle size range 297-595 μm. The sulphation capacity of samples in this test series is given in column 2 of Table 5. As can be seen by comparing columns 1 and 2 some stones do not exhibit any improvement in sulphation capacity with decreased size. In fact, some show a slight decrease which is possibly due to a increased dust loss with the finer particle size. Others such as the Syncrude material show considerable improvement. The effect of particle size on sulphation capacity is of considerable importance in the design of the FBC system and also raises the possibility of improving the performance of sorbents by pelletizing finely ground limestone. These aspects will be the subject of a future report.

THERMOGRAVIMETRIC ANALYSIS

Most of the limestone samples were evaluated by TGA under contract to Dr. Irving Johnson. The sulphation data were obtained on 850-1000 μm (U.S. Sieve) particles precalcined in 20% CO_2/N_2 and sulphated in 0.3% SO_2. A few typical TGA sulphation curves are reproduced in Fig. 11 and 12 along with the fluidized bed reactor generated curves for the same limestones. The shape of the curves from the two methods are very similar.

The sulphtion determined by the TGA tests are given in column 3 of Table 5. With some exceptions the sulphation capacity of the 841-1000 μm samples as determined by the two methods are in reasonable agreement. The average sulphation of 19 samples tested by TGA is 24.2% whereas the average of the same samples determined by the fluidized bed reactor is 21.6%. In both tests Calpo shows up as the best limestone. The largest discrepancies occur with two of the dolomite samples, NS-2 and NB-2 where the fluidized bed results are much lower. Both samples exhibited a significant loss of sample due to thermal shock in the fluidized bed. Both the Glencoe drill cores and Brookfield deposit also produced considerably lower sulphation capacities in the fluidized bed. Most other samples agree within ± 5%.

The differences between the sulphation capacity as determined by the two methods is not surprising considering the different nature of the tests. In the TGA the limestone is brought from room temperature up to 850°C in an atmosphere of 20% CO_2/N_2 which would tend to promote the

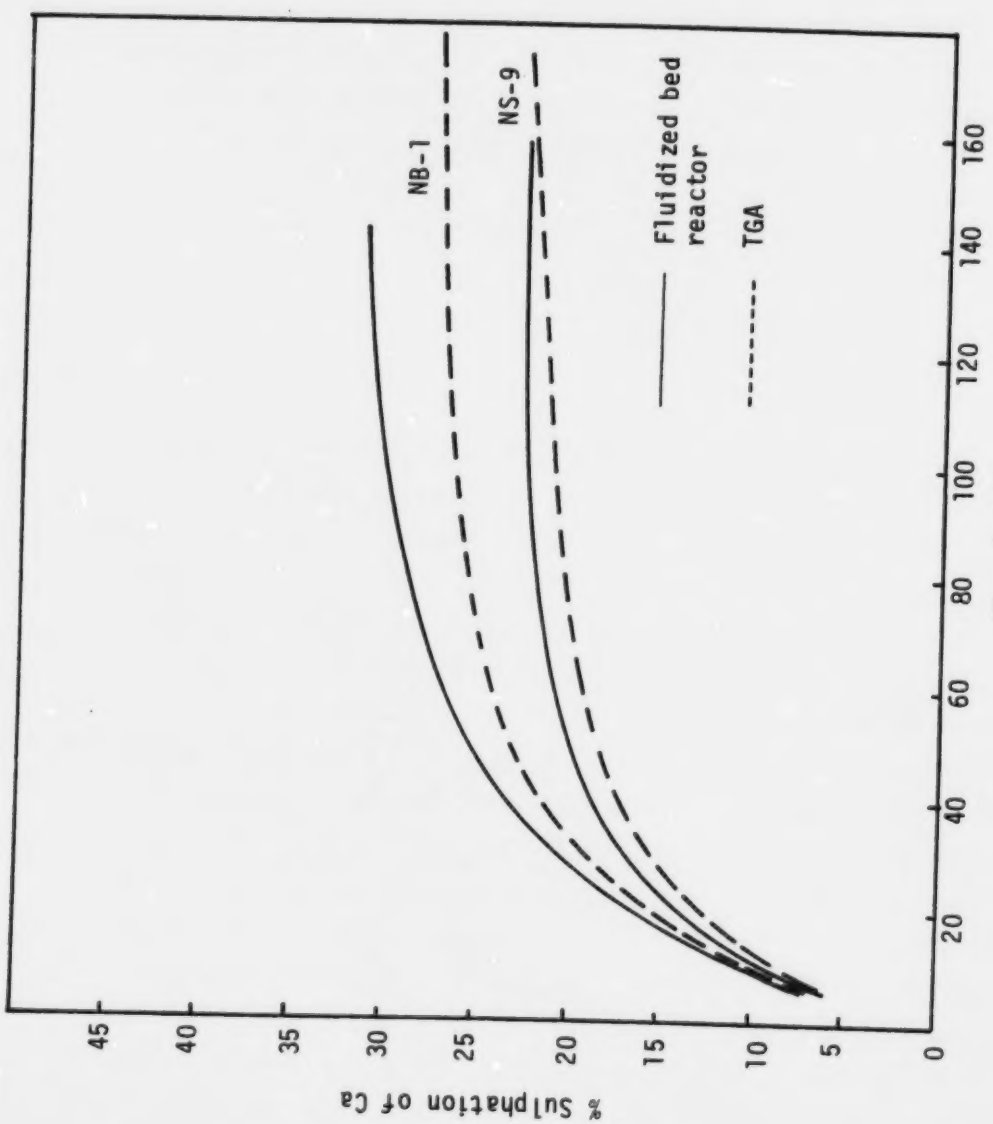

Fig. 11. Comparison of sulphation curves from fluidized bed reactor and TGA data, 0.3% SO_2, 850°C, 841-1000 µm

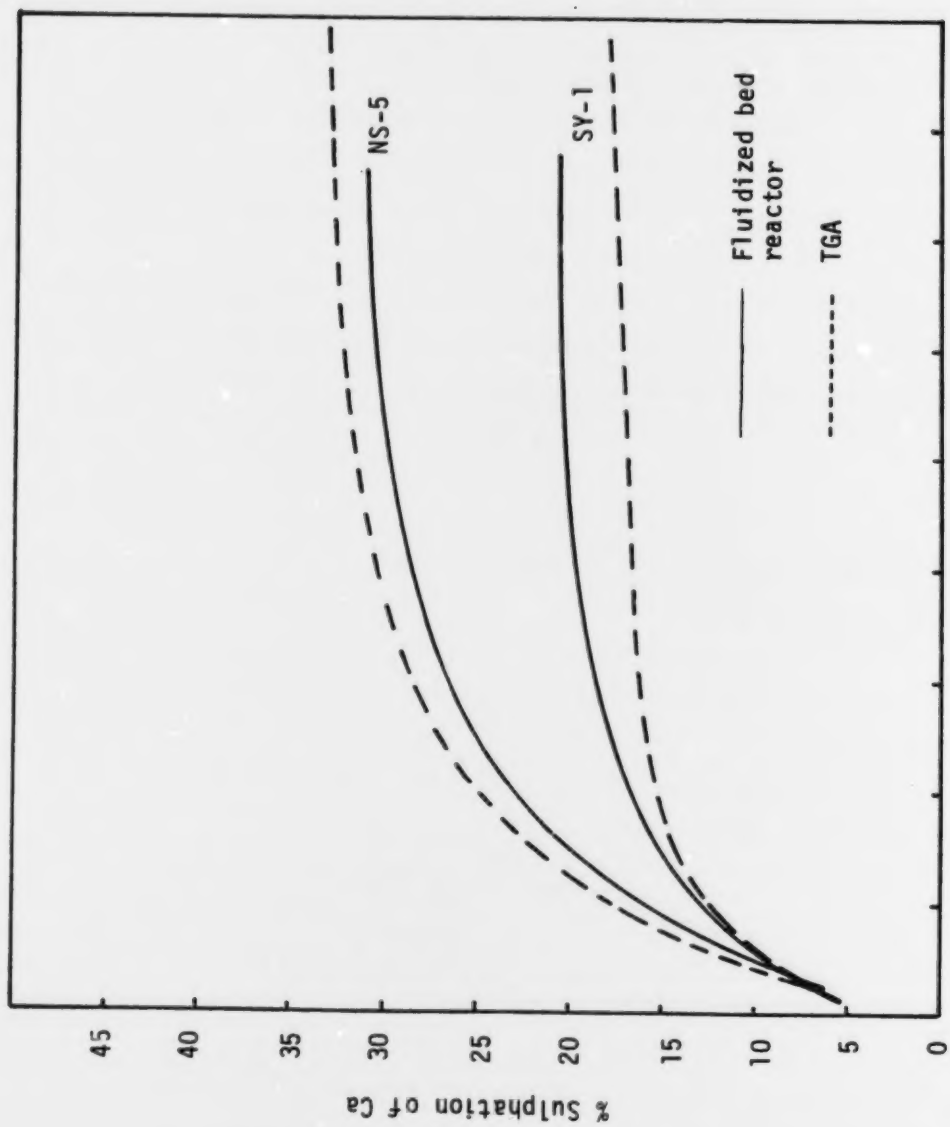

Fig. 12. Comparison of sulphation curves from fluidized bed reactor and TGA data, 0.3% SO_2, 850°C, 841-1000 µm

formation of an open pore structure with subsequent enhanced sulphation capacity. In the fluidized bed the material is subject to thermal shock decrepitation, simultaneous calcination and sulphation as well as attrition during the test run.

CHEMICAL ANALYSIS

Column 4 of Table 5 gives the per cent sulphation as determined from the chemical analysis of calcium and sulphur in the bed material from the 841-1000 μm tests. There was insufficient cyclone material collected for analysis. As mentioned, because the silica made up the bulk of the bed material, it was necessary to separate this from the sulphated limestone prior to analysis. The separation decreases the accuracy of the sulphation determination. The sulphation as determined by chemical analysis is generally higher than that calculated from the fluidized reactor results.

ATTRITION

The susceptability to attrition or breakdown of the limestone by thermal shock, decrepitation, abrasive wear, etc., and subsequent loss of material by elutriation is an important physical property of the limestone. Severe attrition, particularly due to thermal shock, will cause loss of material before it has had time to react with SO_2. Additionally, this could cause difficulties in maintaining a sufficient bed depth and also could overload the cyclone and bag house filters.

As part of his contract, Dr. Johnson performed a shock calcination test to measure decrepitation. In this test 3-4 g of washed and sieved material, 850-1000 μm, was placed in a furnace preheated to 870°C. The stone reached furnace temperature within about 1.5 min. After 20 min it was removed, allowed to cool in air, weighed and sieved through a 850 μm screen. The quantity of material passing the sieve is a measure of the decrepitation.

In the fluidized bed reactor dust from the breakdown of particles is collected by a cyclone on the exhaust line. With a 10 g sample there was insufficient dust to collect accurately. However, in an earlier test series 50 g of 212-841 μm was used and in this case the cyclone dust was collected and weighed. The gas velocity and temperature were constant for all samples. There was a considerable variation in the quantity of dust

collected in replicate tests of the same material. In fact, the weight could vary by a factor of two or more between the high and low figures. The results of the shock calcination test and the attrition in the fluidized bed reactor are given in Table 6.

Table 6 - Attrition test

Sample	Shock Calcination % - 850 µm/initial sample	Fluid Bed Reactor % dust/initial sample
NS-1	0.4	5.5
2	4.9	26.4
3	0.2	2.4
4	0.6	3.2
5	0.2	5.7
6	2.0	7.1
7	0.5	6.1
8	0.3	2.9
9	1.2	3.4
10	0.1	4.9
11	2.6	6.4
12	5.2	7.1
NB-1	0.3	4.6
2	1.1	6.1
3	0.8	19.2
4	3.9	5.5
5	0.1	4.3
CS-1	0.4	0.5
S4-1	0.4	2.0

In the shock calcination tests the highest decrepitation was found for NS-12 (5.2%), NS-2 (4.9%), and NB-4 (3.9%). Although 5% is fairly high for this test, Dr. Johnson did not consider the break-up to be excessive for practical use. The fluidized bed test identified two samples exhibiting much higher than average attrition: NS-2 (26%) and NB-3 (19%); both of which are dolomites. The greater portion of the dust was elutriated within minutes of the sample being injected into the reactor. The dust was composed principally of unreacted material, that is, there was little evidence of sulphation. Table 7 gives the particle size distribution of one of these dolomites compared to a limestone sample which had low attrition. The dolomite dust is much coarser than the limestone.

All the other fluidized bed samples give attrition values of 7% or less. The dust was found to be mostly calcined material and was generally sulphated. The degree of sulphation varied but could equal and occasionally exceed that of the bed material. The agreement between the two methods is not particularly good; NS-2 being the only sample identified as having high attrition in both tests.

Table 7 - Cyclone dust particle size

Size μm	Limestone 6.4% attrition	Dolomite 25% attrition
+176	7.1	19.2
125	19.2	41.6
88	14.9	20.0
62	11.9	9.0
44	12.2	5.0
31	6.1	2.9
22	8.6	0
16	6.3	1.0
11	2.6	0
7.8	5.0	0
5.5	2.8	0.8
3.9	1.1	0.1
2.8	1.6	0

MODELLING

There are a multitude of models for predicting the performance of limestone as SO_2 sorbents during the combustion of coal in FBC (32-39). Normally a model utilizes data from a laboratory test facility such as TGA or bench scale fluidized bed rig and attempts to predict the behaviour of the sorbent in a large scale unit. The mathematics of models can be very complex and the calculations present an onerous task. The real test of any model is, of course, whether it can actually predict limestone requirements versus SO_2 retention for large FBC units. Unfortunately there are very few such units in operation and most comparisons are made against small scale or

pilot FBC's. And often the scatter in the FBC data are so great that any number of model prediction curves could be considered an acceptable fit.

Perhaps the most comprehensive work on modelling has been by Argonne National Laboratory. Reference 32 is a text of over 400 pages with a detailed description of their model and numerous examples of sorbents modelled with TGA data. A number of simple calculations incorporating the physical characteristics of the sorbent and also of the FBC unit being modelled are required to determine the various parameters required by the model. The sulphation data can be used graphically to determine the reaction rate parameter and the maximum utilization parameter as is described in the above reference. Alternatively, the sulphation curve equation can be incorporated in computer program using Laguerre polynominals to solve a numerical integration. This program was acquired from Dr. Johnson. His description of the Argonne model for SO_2 capture in FBC and of the computer program are given as Appendicies 1 and 2. The author has written a program to perform the calculations required by the model which incorporates Dr. Johnson's program. This is given as Appendix 3.

As mentioned, the real test of any model is whether it can actually predict limestone performance in an operating FBC unit. A series of combustion trials with three sizes of Havelock, NB-1, limestone and three superficial fluidizing velocities were conducted in the CCRL pilot scale FBC unit. Each test with a specific particle size and velocity was conducted with and without recycle of cyclone fines back to the bed. The fluidized bed operating conditions and other parameters necessary for the model are given in Table 8.

Fig. 13 to 15 show the actual SO_2 retention versus Ca/S mole ratio for pilot FBC tests using the three sorbent sizes. The solid data points are for tests with no cyclone dust recycle. The predicted model curves are in reasonable agreement with the actual test results. The model does not have the ability to take the recycle of cyclone dust into account. It has a tendancy to slightly overpredict the retention with no recycle and to under-predict where there is recycle. Also plotted on Fig. 13 is the model prediction based upon the TGA sulphation curve. It falls slightly below that of the fluid bed reactor, the reason being that the sulphation capcity found by the TGA was 28.4% compared to 30.3% for the reactor. Both the

Table 8 - CCRL pilot FBC operating conditions

Temperature = 850°C
Pressure = 101 kPa
Fluidizing velocity = 1.22, 2.13, 3.05 m/s
Static bed height = 0.46 m
Expanded bed height = 0.66 m
Area of bed = 0.155 m
Number of openings in distributor = 400
Coal feed rate = variable from 22 to 58 kg/h
Sulphur content in coal = variable from 2.9 to 5.0%
Sorbent = Havelock, NB-1, limestone
Calcium content = 95% $CaCO_3$
Sorbent particle size = 6*20M :ave 1.216 mm, 1/4*0M : ave 1.600 mm, 1/4*20M : ave 2.39 mm
Sorbent bulk density = 1.45 g/cc (6*20M)
Sorbent particle density = 2.53 g/cc
Sulphation curve equation : a=30.30, k=0.05364, n=0.8399
FB Reactor SO_2 concentration = 2625 ppm

model and the test results indicate that the fluidizing velocity has very little effect on the SO_2 retention. Sorbent particle size appears to be the parameter which has the greatest effect on SO_2 retention with Ca/S ratio.

In the case of Havelock limestone, NB-1, the parameters of the sulphation curves generated by the TGA and fluidized bed reactor are very similar. As mentioned earlier, it was found that a 10 g sample in the fluidized bed reactor produced this desired result. Table 9 shows the effect of sample weight on the parameters of the sulphation equation. It also indicates the degree of reproduceability of the sulphation capacity in the value of "a". Table 10 gives the sulphation curve parameters "a", "k", and "n" for all the sorbent samples which were tested by both methods. Where the sulphation capacity, that is "X" or "a", are approximately the same in both tests, then the model prediction curves are in reasonable agreement. This is the situation for samples of NS-5, -6, -9, NB-1, -2, and SY-1 where, for example, at a Ca/S of 5 the SO_2 retention for the two methods agrees within about 5%. In most of the other samples there is fair agreement between the two methods. In general, although the sulphation capacity of the fluidized bed reactor method is lower than the TGA, the parameters "k" and "n" are such that the fluidized bed reactor model

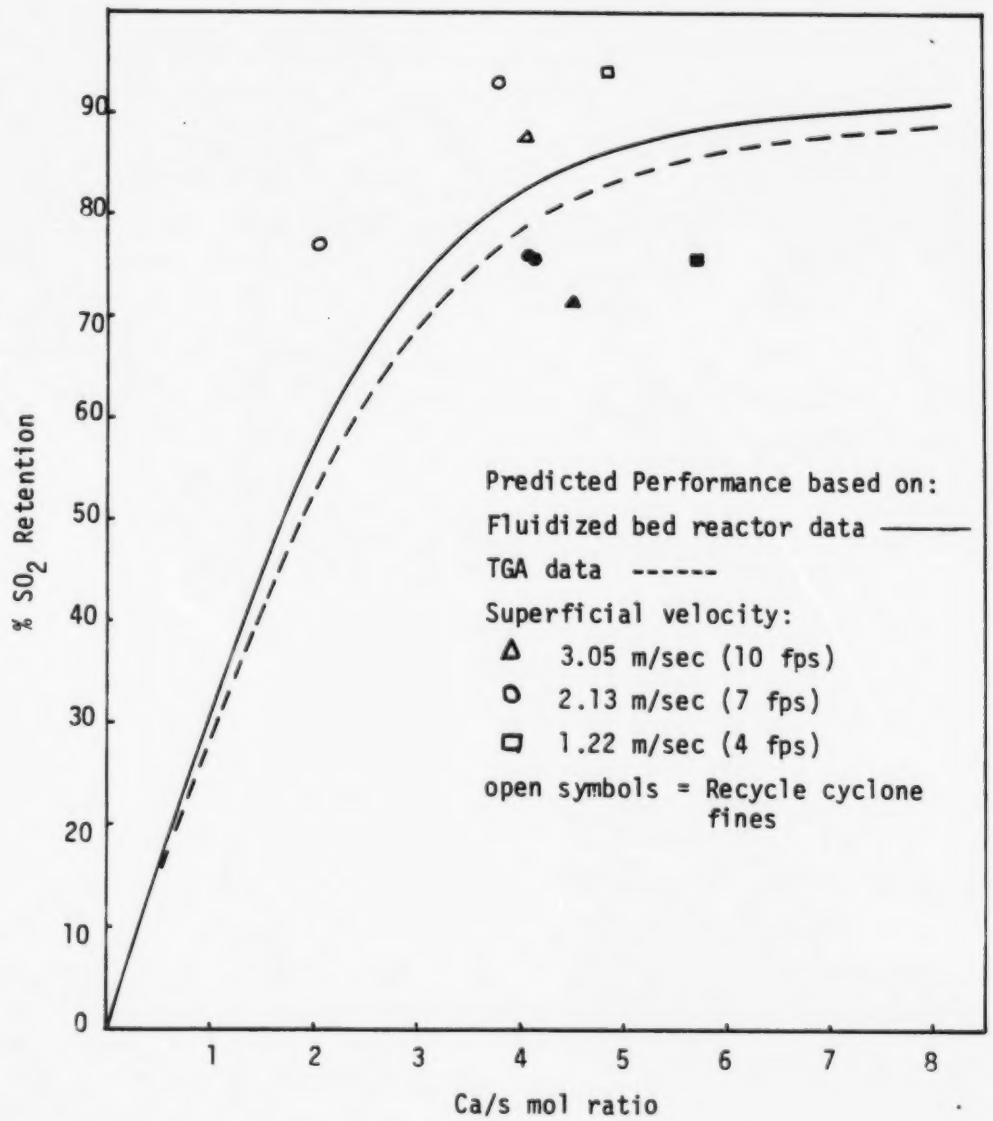

Fig. 13. Performance of Havelock limestone (NB-1), -6.3 mm size, in the CCRL AFBC.

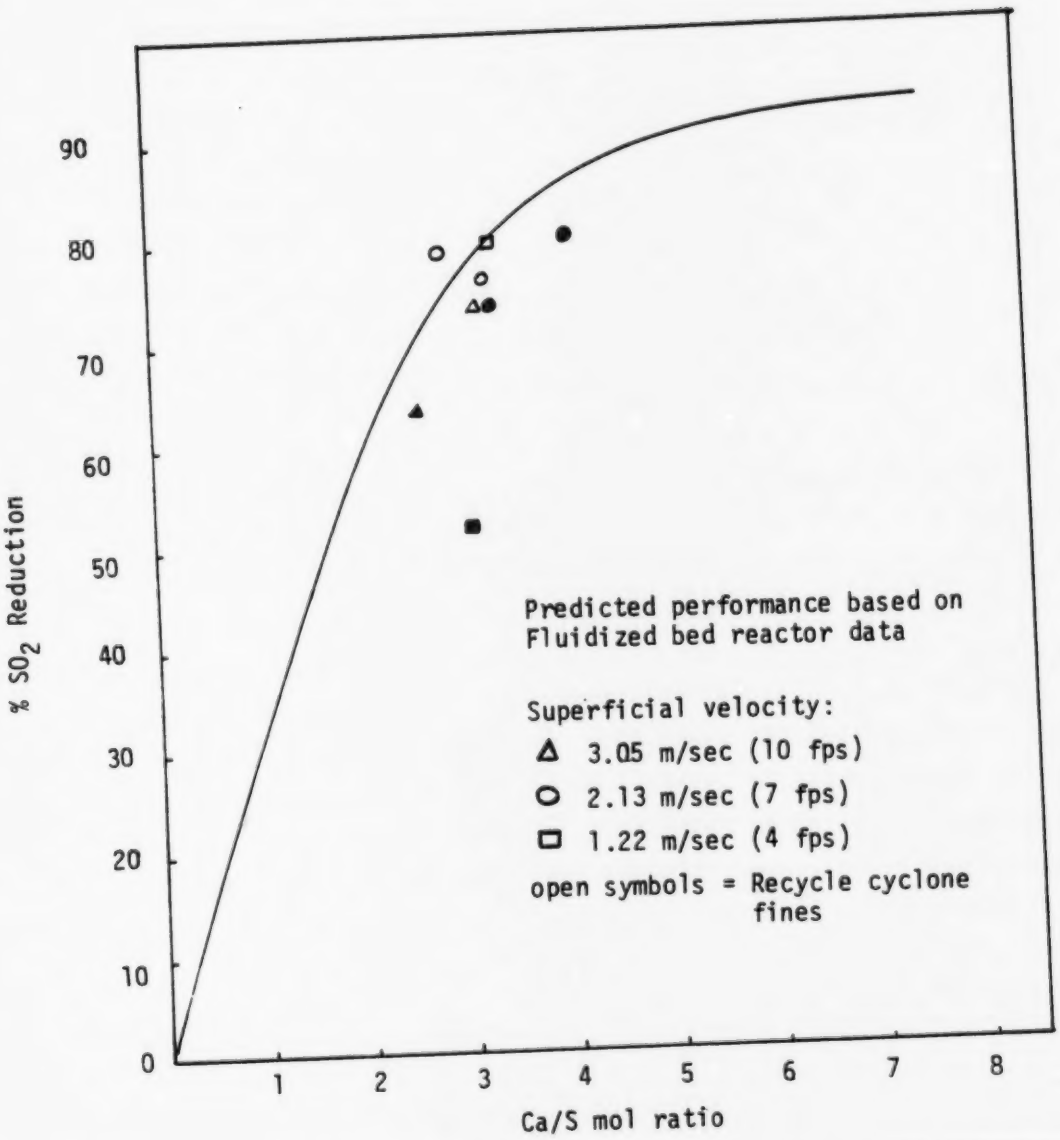

Fig. 14. Performance of Havelock limestone (NB-1), 0.841-3.36 mm, in the CCRL AFBC.

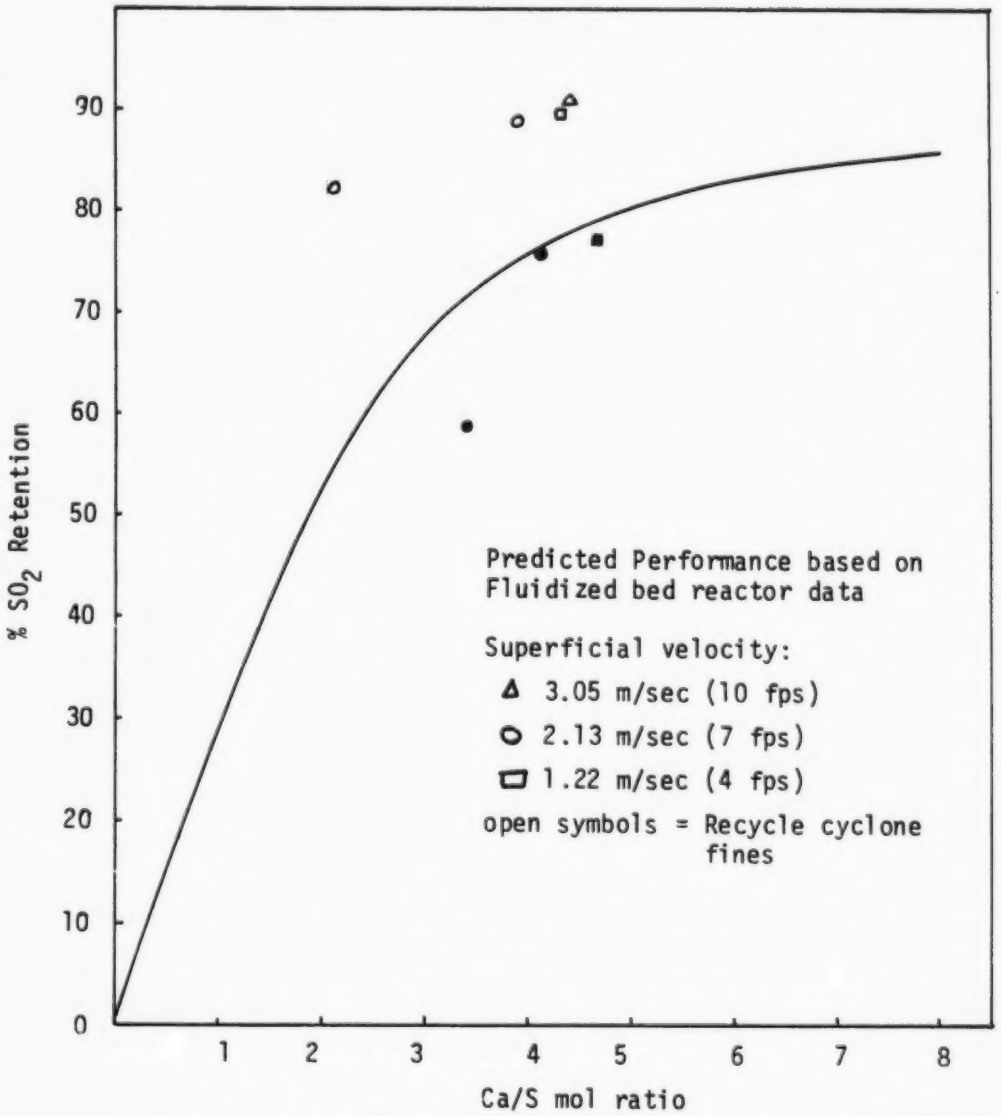

Fig. 15. Performance of Havelock limestone (NB-1), 0.841-6.3 mm, in CCRL AFBC

prediction curve is steeper than that of the TGA. Consquently the fluidized bed usually predicts a better SO_2 retention for a given Ca/S ratio than does the TGA. As it is reported that the TGA method generally underpredicts the SO_2 retention (32), the fluidized bed data should result in a better prediction.

Table 9 - Effect of sample weight on sulphation curve parameters for Havelock NB-1 limestone

Sample weight	"a"	"k"	"n"
50 g	29.139	.01345	1.0275
35 g	29.973	.02137	1.0027
25 g	29.160	.03209	.9466
20 g	31.072	.03437	.8601
10 g	31.402	.05364	.8399
10 g	32.338	.05894	.8369
TGA	28.38	.05372	.8831

Table 10 - Sulphation curve parameters

Sample	TGA				Fluid Bed Reactor				
	X	a	k	n	X	a	k	n	P_2
NS-1	20.5	20.33	.0944	.705	25.48	25.160	.06903	.8603	2600
9	24.78	25.16	.1244	.5875	22.44	22.767	.06695	.8919	2700
2	22.37	26.61	.2416	.3796	11.38	8.949	.06126	.2019	2850
3	25.7	25.49	.2085	.5453	21.08	22.533	.12804	.6545	2550
13									
4	16.7	17.31	.6226	.2442	10.53	10.572	.14579	.9098	2700
8	19.81	19.57	.0913	.8633	12.24	12.43	.13071	.8160	2750
5	33.80	33.58	.0650	.8317	31.79	31.577	.05330	.8695	2650
10	42.09	41.14	.02768	.9862	46.15	47.126	.04337	.8474	2790
6	25.5	26.23	.2556	.4564	21.28	23.544	.09679	.7669	2350
7	24.93	24.50	.0796	.7998	20.47	21.633	.08374	.6750	2675
11	26.31	26.46	.1507	.5746	16.20	16.120	.13337	.7169	2450
12	23.59	24.14	.1634	.5206	14.80	14.238	.10893	.8294	2750
NB-1	29.94	28.38	.05372	.8831	30.65	30.59	.05629	.8384	2625
2	20.79	21.97	.4995	.2818	22.97	24.013	.07564	.7693	2850
3	31.35	46.97	.1436	.3656	19.47	19.569	.1450	.9086	2800
4	14.15	14.64	.2851	.4596	17.21	17.857	.09749	.7688	2850
5	17.66	17.53	.1083	.6996	20.34	20.702	.08155	.8102	2515
CS-1	21.76	21.26	.0956	.7264	25.67	26.429	.04603	.9522	2475
SY-1	19.31	18.87	.1467	.6293	20.64	21.038	.08763	.7828	2450
2					22.26	22.450	.07796	.9669	2750

PREDICTED SORBENT UTILIZATION FOR SUMMERSIDE FBC

As the Summerside unit is the largest FBC in operation in Canada it was chosen for comparison of all the sorbents. The physical characteristics of the unit are given in Table 11. Figs. 16 to 19 are the predicted SO_2 retention versus the Ca/S mole ratio. Figs. 20 to 22 show the prediction curves expressed as SO_2 retention versus the kg of sorbent required per kg of 4.1% S coal. These latter curves are more useful in determining the relative ranking of sorbents. Calpo, NS-5 and -10, is the best sorbent. Those sorbents which require more than 1.0 kg/kg coal and still do not achieve 80-85% SO_2 retention should probably not be even considered for use in FBC. For the other sorbents these curves plus knowledge of the availability, cost and transportation should enable the user to choose the most economical sorbent for his requirements.

Table 11 - Summerside FBC operating conditions

Temperature = 850°C
Pressure = 101 kPa
Fluidizing velocity = 1.83 m/s
Static bed height = 0.6 m
Expanded bed height = 1.5 m
Area of bed = 3.52 sq. m (A bed), 3.96 sq. m (B bed)
Number of openings in distributor = 284 (A bed), 472 (B bed)
Coal feed rate = 1100 kg/bed
Sulphur content in coal = 4.1%
Sorbent particle size = 6*20 M : ave 1.240 mm

LIMITATIONS OF THE MODEL

As shown above, the model is useful in determining the relative ranking of a series of sorbents. It can also give a reasonable indication of the expected performnace of a sorbent in an FBC as shown with the CCRL trials. However there are certain caveats associated with its use. In the experiments to obtain the sulphation curves the sorbent particle size used is 841-1000 μm and it is assumed that sorbent in the bed will sulphate in the same manner. It also assumes that the mass weighted average particle size of the bed in fact represents the behaviour of all the particles in the bed. Providing that particle size distribution in the bed is not too wide,

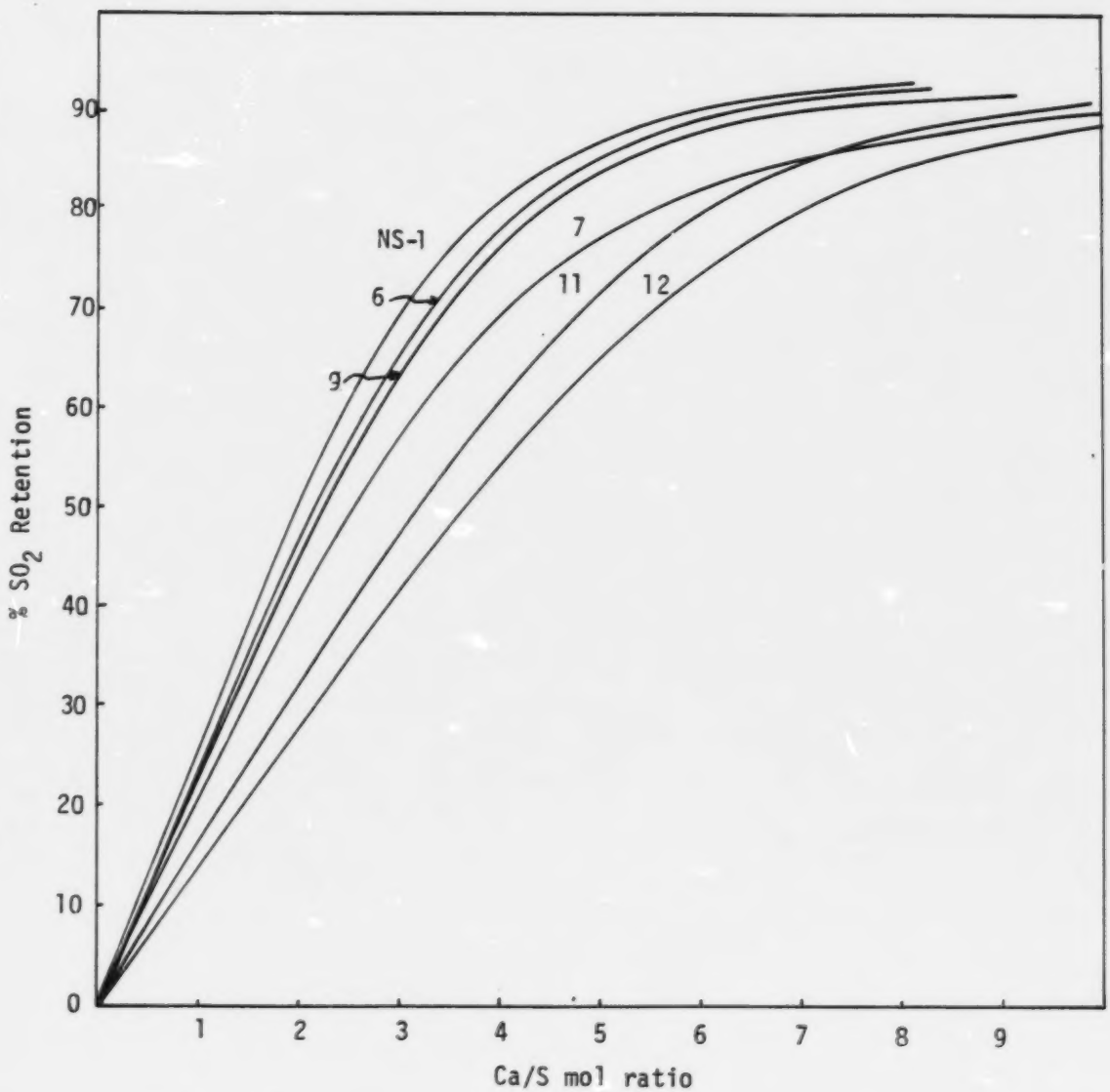

Fig. 16. Predicted performance of Nova Scotia sorbents in the Summerside AFBC

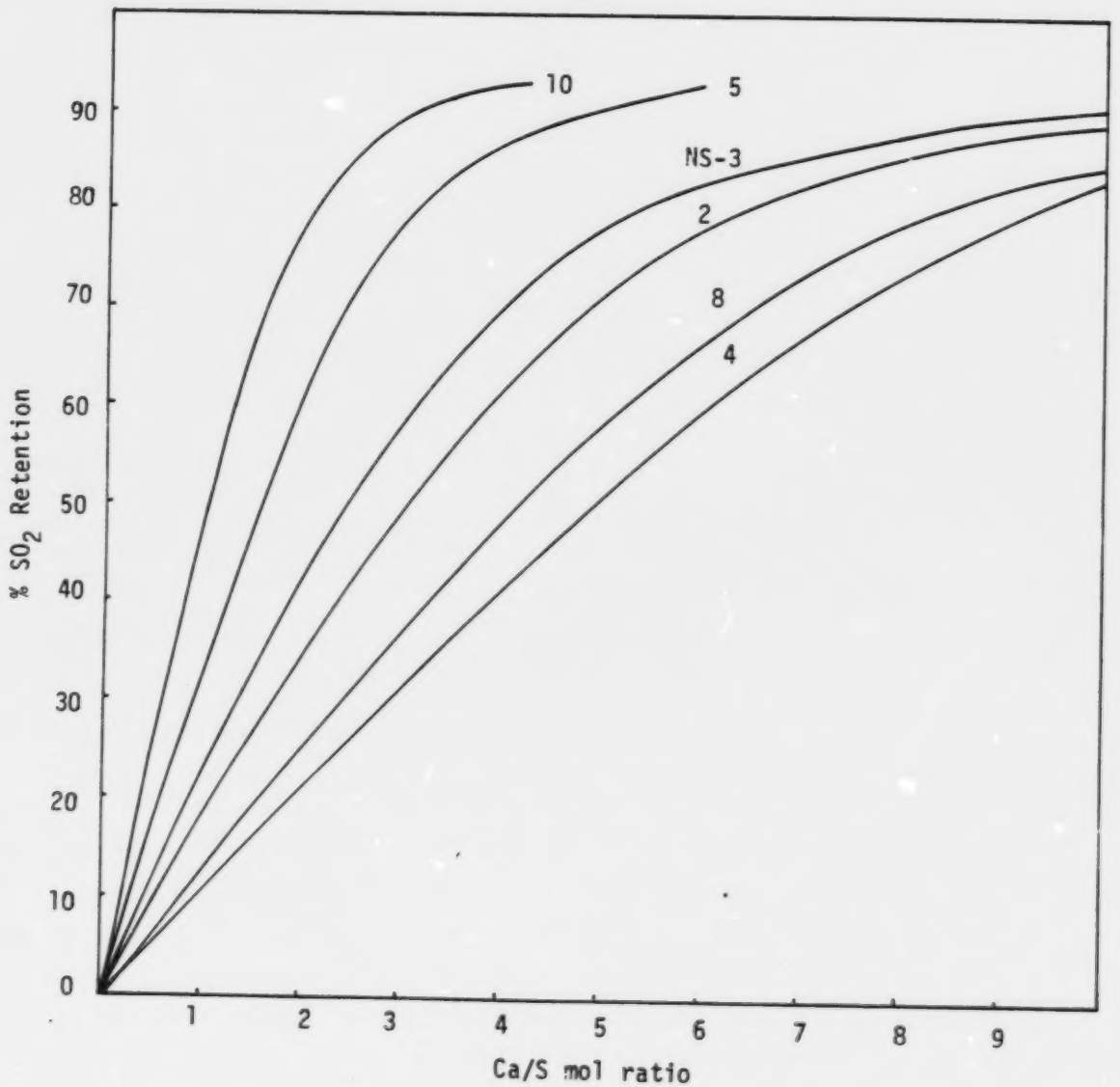

Fig. 17. Predicted performance of Nova Scotia sorbents in the Summerside AFBC

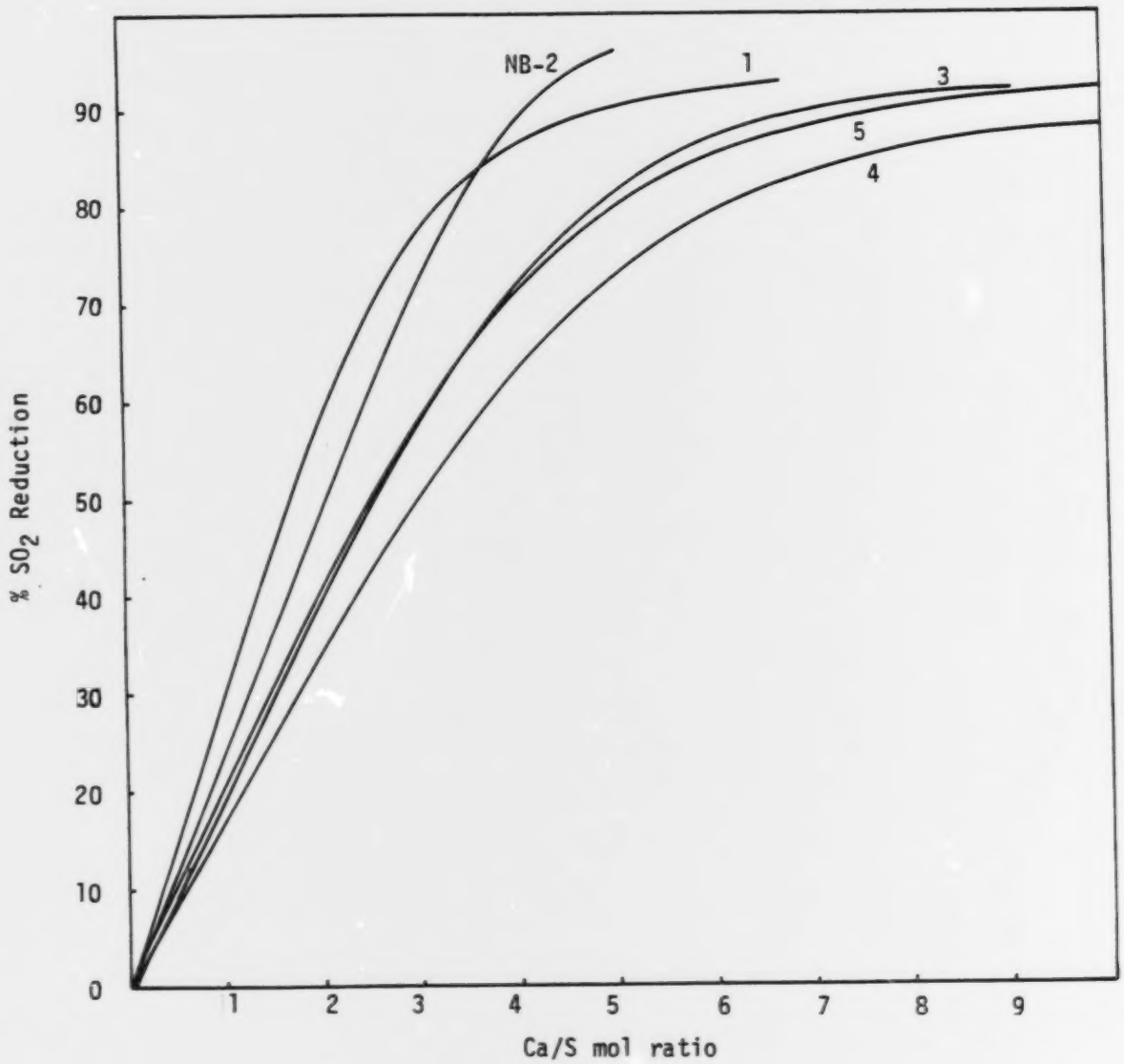

Fig. 18. Predicted performance of New Brunswick sorbents in the Summerside AFBC

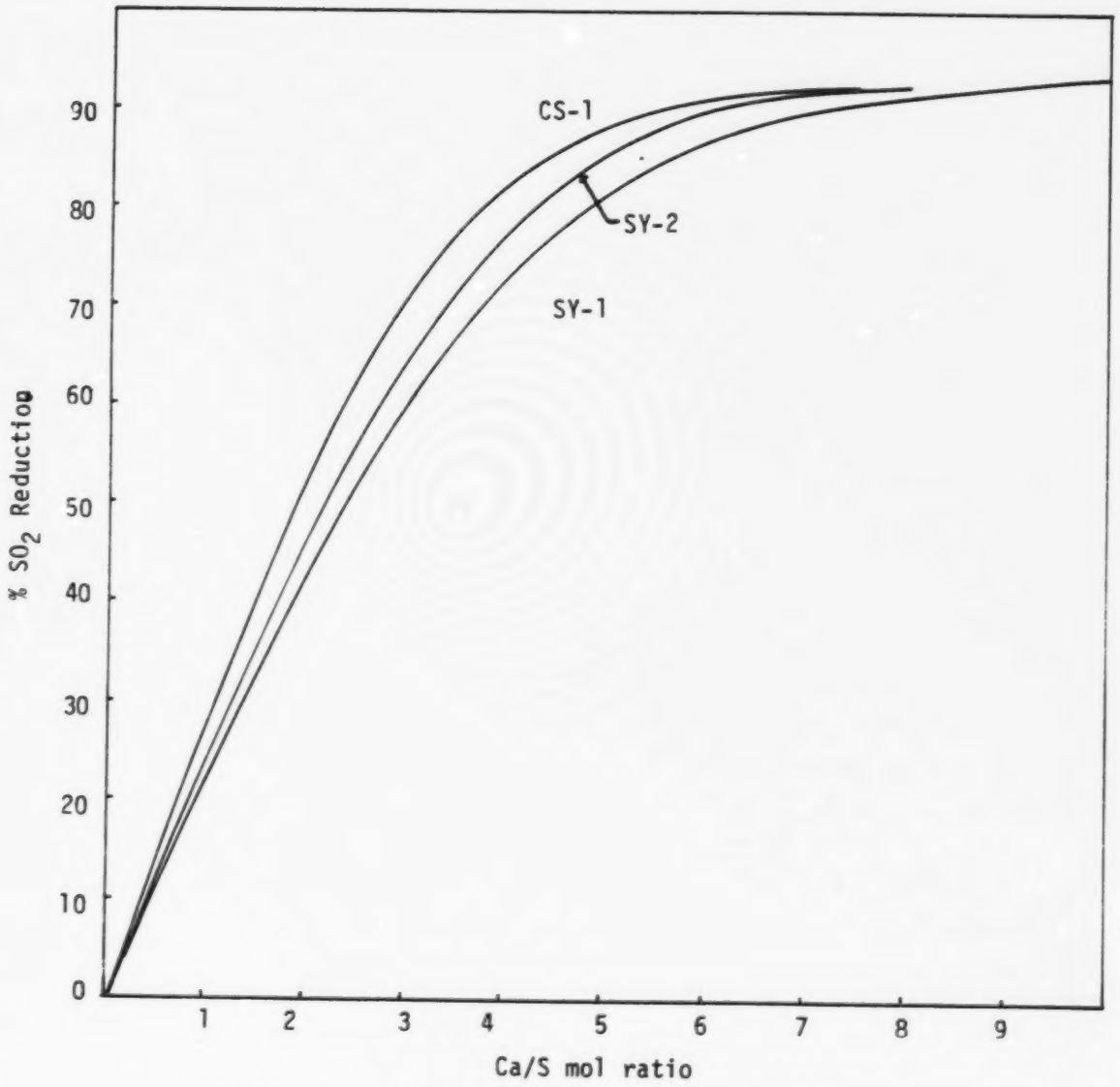

Fig. 19. Predicted performance of Alberta sorbents in the Summerside AFBC

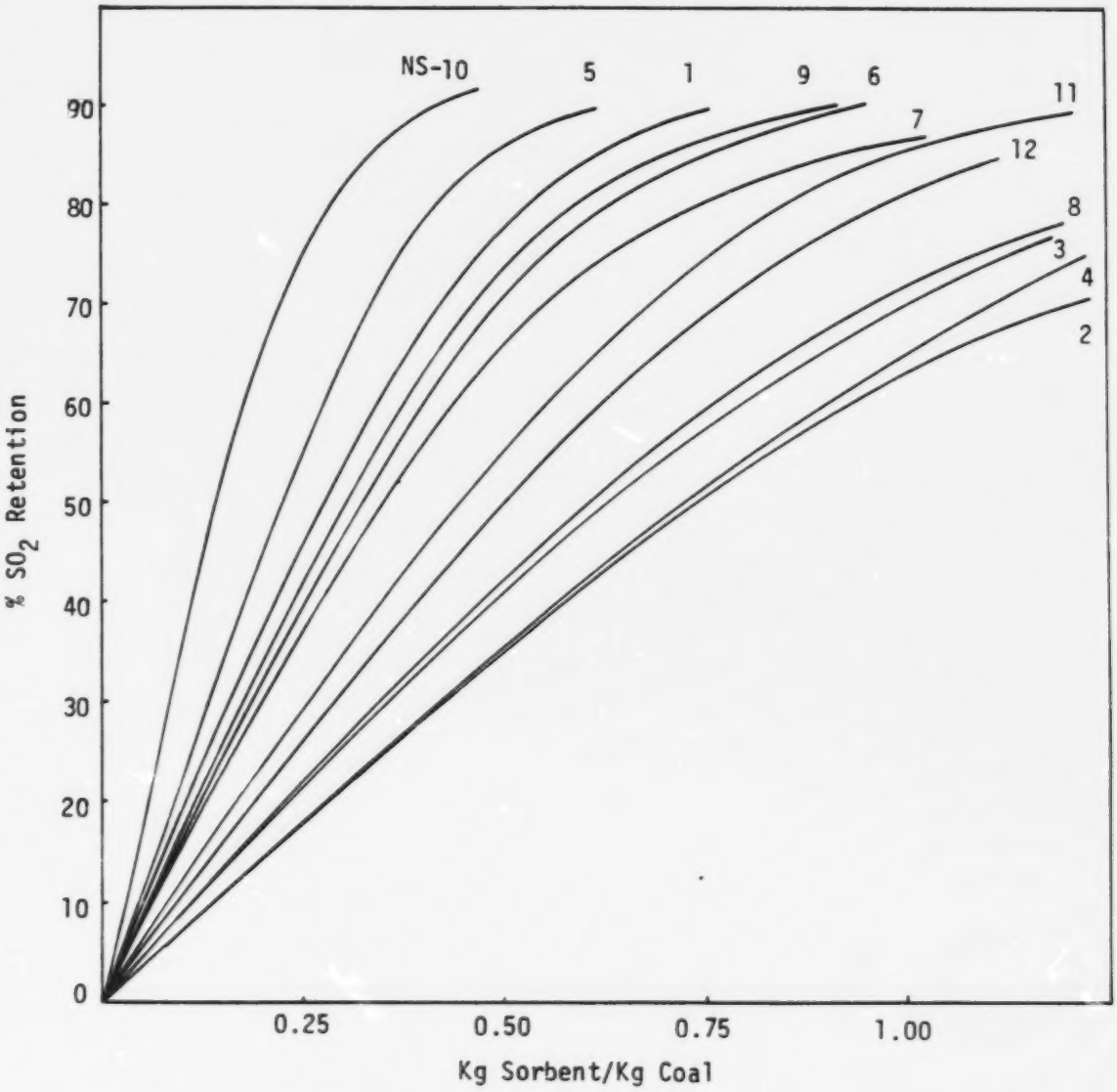

Fig. 20. Predicted quantity of Nova Scotia sorbent required for the Summerside AFBC combusting 4.1% S coal

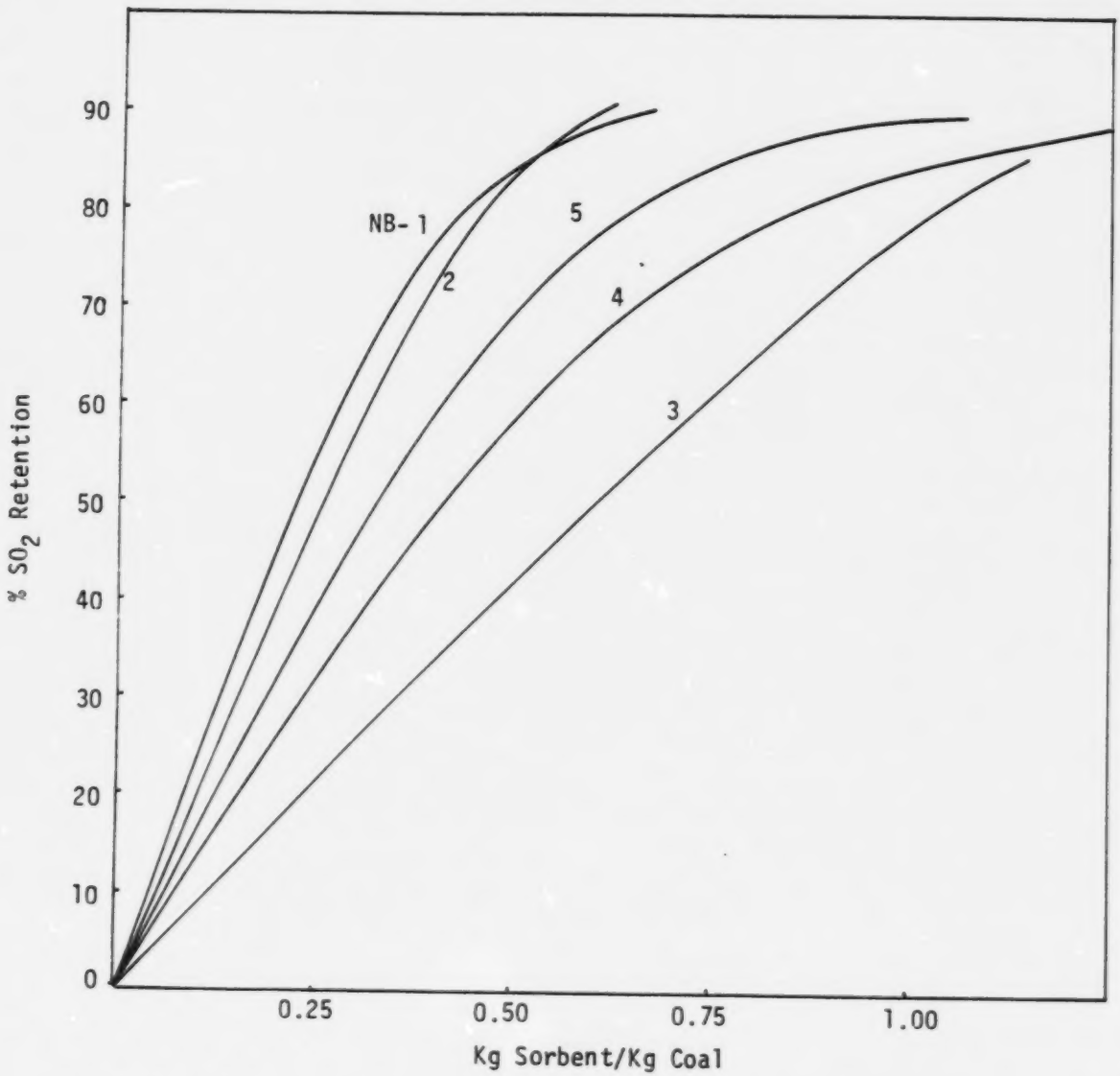

Fig. 21. Predicted quantity of New Brunswick sorbent required for the Summerside AFBC combusting 4.1% S coal

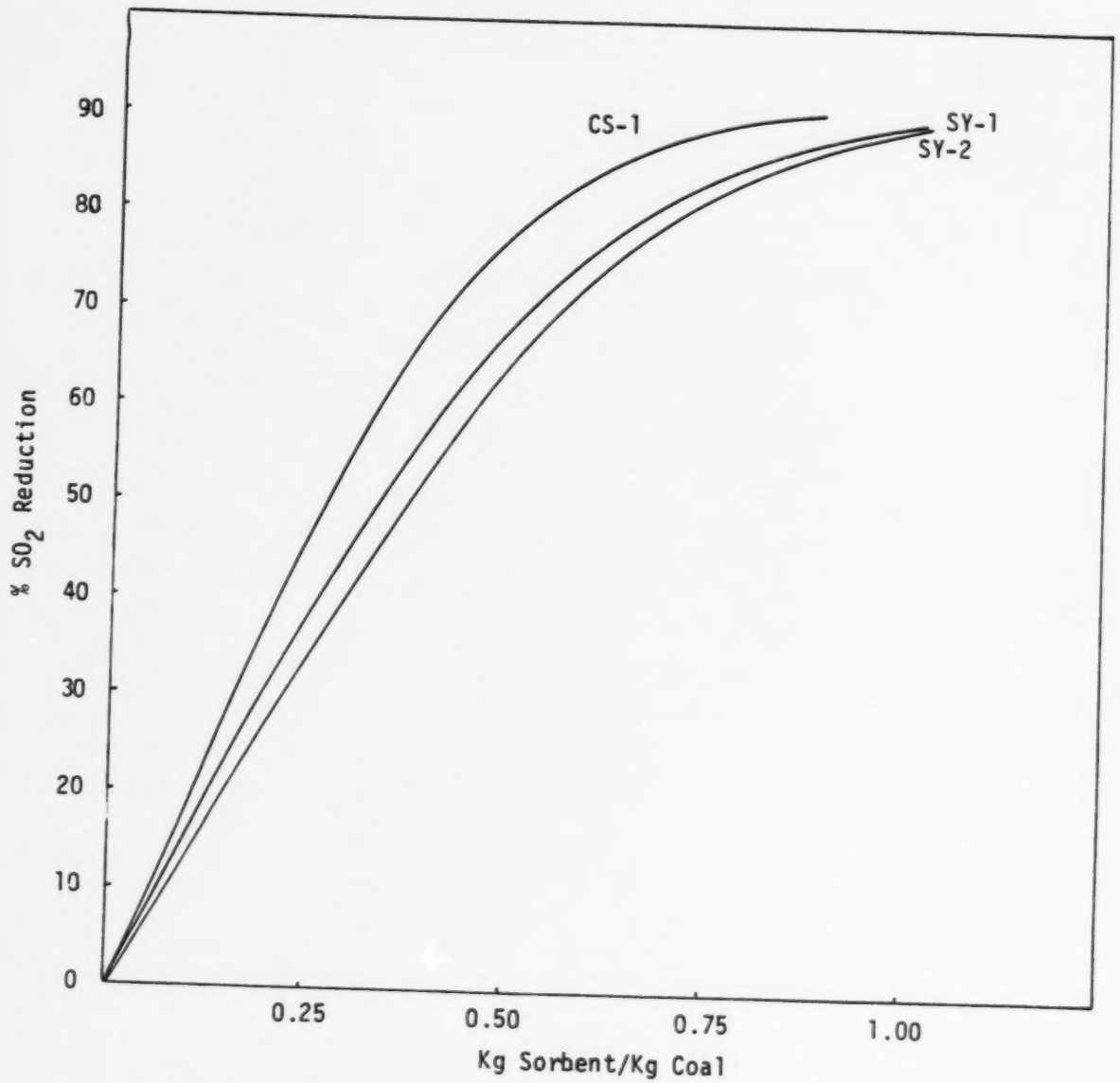

Fig. 22. Predicted quantity of Alberta sorbent required for the Summerside AFBC combusting 4.1% S coal

that the average size is not too dissimilar to that of the test and that the sorbent's sulphation capacity is not greatly dependant upon size, then the assumption is valid. However, as was discussed in the section on particle size, the sulphation of some limestones are quite dependant on particle size and in this case the model will be inaccurate.

The model does not take into account the beneficial effect of recycling cyclone fines back to the bed. Consequently it will overpredict limestone requirements in this case. It also assumes that all the sulphur dioxide capture takes place in the bed whereas in fact some capture does occur in the freeboard. Argonne has developed an addition to the basic model which does calculate the freeboard sulphation (32). It indicates that the freeboard captures only 9-10% of the total sulphur fed to the bed. Because this not a large amount and would not change the relative ranking of the sorbents it was not included in this report.

As can be viewed in the model prediction curves, large increases in Ca/S ratio yield only a small increase in SO_2 retention in the 80-90% range due to the flat nature of the curve in this region. Consequently, the model tends, particularly with the TGA data, to overpredict limestone requirements for the high SO_2 retentions.

There are indications that limestone sulphation behaviour may be significantly influenced by the characteristics of the coal ash (32). Argonne reports that the maximum sulphation was increased by 40% when a limestone was mixed with coal ash in the TGA compared to a test with no ash. It is possible that the alkali in the ash may improve the pore structure of the sorbent and that the iron oxides may have a beneficial effect as a catalyst. In the fluidized bed reactor the bed material was pure silica sand. In some preliminary tests half of this sand was replaced by ash from the combustion of interseam coal partings from the Highvale, Alberta open pit mine. The effect was a 28% reduction in the sulphation capacity of Havelock, NB-1, and a 21% reduction for Irish Cove, NS-9. Thus it would appear that although ash may have an effect on sulphation capacity, it is not always a positive one. The influence of coal ash will be investigated further and covered in a later report.

CONCLUSIONS

This first report on sorbent utilization has presented data from a series of tests on limestones and dolomites from Nova Scotia, New Brunswick and Alberta. A total of 29 samples were sulphated in an experimental fluidized bed reactor and 19 of the samples were also tested by TGA. There is an approximate fourfold difference in the sulphation capacity from the worst sorbent to the best. There can even be a considerable difference in performance between samples from the same geological deposit. The best limestone is that from the Calpo deposit in Antigonish, N.S. Contrary to expectations based on the literature, the dolomite samples test results were only fair to poor. Some of the limestone and dolomite samples had such a low sulphation capacity that they would be completely unsuitable for use in FBC.

The test results of the fluidized bed reactor and the TGA are with some exceptions in reasonable agreement. It remains to be seen which is the more accurate. Using the sulphation data and the Argonne National Laboratory model the behaviour of the limestone samples was predicted for the CCRL and Summerside FBC units. The model agreed well with actual data from CCRL combustion tests. With the model prediction curves it was possible to rank all of the sorbents tested.

In future work the effect of the coal ash on the sulphation capacity of sorbents will be investigated. Work will be done in an attempt to improve the performance of the sorbent by pelletizing finely ground limestones.

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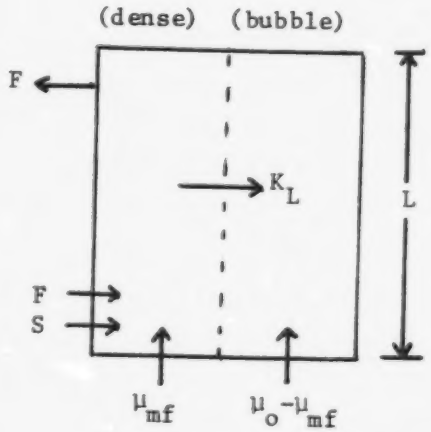
APPENDIX 1

ARGONNE MODEL FOR SO_2 CAPTURE IN FBC

Examination of the data for SO_2 capture in a FBC shows that the fraction of SO_2 generated by the oxidation of the sulfur in the coal that is retained in the bed depends on the following variables: (1) the ratio of the number of moles of calcium fed to the number of moles of sulfur fed to the combustor, (2) the superficial velocity of the fluidization air, (3) the reactivity and the type of limestone, (5) the temperature, and, (6) the pressure. An understanding of these observations can be obtained by means of a simple model for the sulfur capture. This steady state model for the sulfur capture assumes that the fluidized bed can be represented by the two-phase model, i.e. a dense phase and a bubble phase, that the SO_2 is generated in the dense phase (in which most of the coal combustion takes place), that the solids and the gases in the dense phase are completely mixed, that the bubbles are in plug flow and that the SO_2-limestone reaction in the FBC in controlled by the same factors that control the reaction when carried out in the laboratory. It is assumed that by the proper choice of particle size and temperature in the laboratory experiments that the influence of these variables on the FBC process can be taken into account.

The sulfur balance may be written:

$$S = C_1 G_1 + C_2 G_2 + Fx \qquad (1)$$



where:

- S = sulfur feed rate, moles/sec
- C_1 = SO_2 conc. in dense phase, moles/cm^3
- C_2 = SO_2 conc. in bubble as it leaves
- G_1 = Gas flow rate, dense phase, cm^3/sec
- G_2 = Gas flow rate, bubble phase, cm^3/sec
- F = Calcium flow rate, moles/sec
- x = Ave fractional sulfation of stone leaving the bed.

Examination of the diagram shows that:

$$G_1 = A\, u_{mf} \quad \text{and} \quad G_2 = A\,(u_o - u_{mf}) \tag{2}$$

where A is the bed cross-sectional area, u_o the superficial air velocity and u_{mf} the minimum fluidization velocity. It is assumed that C_1, the SO_2 concentration in the dense phase is constant. The SO_2 concentration in the bubble phase increases from zero at the bottom of the bed to some higher value at the top of the bed. If plug flow of the bubble phase is assumed, it may be shown that the value of C_2 as the gas leaves the bed is given by:

$$C_2 = C_1(1 - \exp(-k_L\delta\ L/(u_o - u_{mf}))) \tag{3}$$

where:

K_L = SO_2 exchange rate constant between dense and bubble phases
δ = volume fraction of bubbles in the bed
L = bed height

When these expressions are substituted into the sulfur balance equation the result may be written:

$$S = C_1 G + Fx \tag{4}$$

in which,

$$G = A\, u_{mf} + A(u_o - u_{mf})(1 - \exp(-k_L\delta\ L/(u_o - u_{mf}))) \tag{5}$$

The quantity G is in effect a gas flow rate (cm^2/sec). Three cases may be considered. If $k_L = 0$, i.e. no transfer of SO_2 to the bubble phase, than $G = Au_{mf}$ and the smallest value for G would be obtained. The highest retention would be obtained since no SO_2 would be lost to the bubble phase. On the other hand if $k_L \to \infty$ then $G \to Au_o$ and the whole gas flow through the system would dilute the SO_2 and the lowest retention would be obtained. The real case is between these two extremes and is closer to the $k_L = 0$ limit.

The average fractional sulfation of the limestone which leaves the bed, x, may be calculated using the relation:

$$x = \int_0^\infty E(t)\, x(t)dt \tag{6}$$

where E(t) is the age distribution function for the material that leaves the bed and x(t) the dependence of the fractional sulfation on time as determined from the laboratory sulfation experiments. It may be shown that for a completely mixed system that:

$$E(t) = (\tfrac{1}{\tau})\exp(-t/\tau) \tag{7}$$

where:

τ = residence time for the solids in the bed

$$\tau = B/F \tag{8}$$

where B = the calcium content (moles) of the bed. The conversion, x is given by the equation:

$$x(t) = a(1-\exp(-kt^n)) \tag{9}$$

where a, k and n are empirical constants. The constants a and n are specific for each limestone but do not have a significant dependence on the SO_2 concentration. The constant k varies with the SO_2 concentration--

$$k = k\, C^n SO_2 . \tag{10}$$

When these expressions for x(t) arc substituted into the sulfur balance equation one obtains:

$$S = C_1 G + F \int_0^\infty (1/\tau)\exp(-t/\tau)\, a(1-\exp(-k'(C_1 t)^n))dt \tag{11}$$

To use this equation a numerical integration method is needed. Because of the dependence of x(t) on C_l, the solution of Eqn (11) must be obtained using an interative method. When a solution has been obtained, the sulfur retention in the bed may be computed from x and the Ca/s mole ratio:

$$\text{Retention} = (Ca/S)\, x. \qquad (12)$$

Note that the Ca/s mole ratio is equal to F/S.

Prepared 17 September 1980
by Irving Johnson

APPENDIX 2

Program SO_2 FBI

by

Irving Johnson

The program begins by requesting the input of values for the empirical constants of the sulphation equation (a, K_2, and N) and the combustor conditions (S, the sulphur feed rate, B, the calcium content of the bed, and G, the effective gas flow rate).

After some DATA statements for the subscripted variables Y(I) and W(I), (explained below) the value for the SO_2 concentration used in the sulphation experiments (3000 ppm) are entered as data. The initial value of K_2 corresponds to this value of the SO_2 concentration.

The first DO loop (J=2, 20) is used to compute a series of values of the calcium feed rate, C, and the residence time, R. A key element of this program is the numerical method used to evaluate the integral for the utilization, x, (sulphation):

$$x = \int (1/\tau)\exp(-t/\tau)a(1 - \exp(-kt^{**}n))\, dt$$

The substitution $y = t/\tau$ is made to yield the result:

$$x = \int \exp(-x)f(x)dx = \sum_{i=1}^{m} w(i)f(x(i))$$

This integral is numerically evaluated using Laguerre polynominals as described in the Handbook of Mathematical Functions (N.B.S. Applied Mathematical Series 55) pages 890 and 923. This method approximates the integral with a series:

$$\int \exp(-x)f(x)dx = \sum_{i=1}^{m} w(i)f(x(i))$$

where the w's and x's are computed from Laguerre polynominals.

The values of Y(I) and W(I) given in the DATA statement of the program are for m = 10 (the limit on the second DO loop).

The constant $k_r{}^n$ (K*(R**N)) is evaluated and then the integral computed to obtain the average utilization x, (Z in program). The exit SO_2 concentration (in ppm) is computed from the material balance equations (eqn 4 or 11 in the appendix). If the value of P1 is close enought to the initial value, the retention is printed out beginning at 60 in the program. If the two values (P1 and P) are not close enough, a new value of P is estimated by taking the geometric mean of the two values. It is possible for P1 to be negative, in which case one-half of the initial value is used to estimate the new quess. A new value of K is computed, corresponding to the new value for the SO_2 concentration. The utilization is again computed and the comparison repeated. A counter, L, is used to restrict the number of iterations to 100. This usually stops the program when the retentions reach values greater than 90%.

APPENDIX 3

MICROSOFT BASIC PROGRAM FOR ANL MODEL FOR FBC BY C.A. HAMER

```
100 CS$=CHR$(4)
110 PRINT CS$:RO$=CHR$(1):RF$=CHR$(2)
120 PRINT"     ";:PRINT RO$;
130 PRINT"* * * THIS PROGRAM CALCULATES THE PARAMETERS FOR FBCSO2 MODEL * * *"
140 REM * THIS IS THE ARGONNE NATIONAL LABORATORY MODEL FOR FBC
150 REM * REFERENCE ANL REPORTS : ANL/CEN/FE-80-17 AND ANL/FE-80-10
160 REM * THIS PROGRAM BY C.A.HAMER, CANMET
170 PRINT RF$:PRINT:PRINT
180 PRINT")) These parameters are: SULPHUR FEED RATE: S; QUANTITY OF CALCIUM IN THE"
190 PRINT"   BED: B; and the EFFECTIVE GAS FLOW RATE: G. Do you want to CALCULATE"
200 PRINT"        these parameters (Y OR N)";:INPUT R$
210 IF R$="Y" THEN 220 ELSE 1550
220 PRINT CS$:PRINT")) What is today's date (DD MM YY)";:INPUT D$:PRINT
230 LPRINT"TODAY'S DATE ";D$
240 PRINT")) In order to calculate S,B and G, it is necessary to provide"
250 PRINT"   the physical parameters  of the limestone and the FBC unit you "
260 PRINT"   wish to model. Please answer the following questions:":PRINT
270 PRINT")) The following calculations assume an FBC temperature of 850C"
280 PRINT"   If you want calculations at a different temperature you must"
290 PRINT"   give the density and viscosity of air at the desired temperature"
300 PRINT"   Do you want the calculations at 850C Y OR N";:INPUT R$
310 IF R$="Y" GOTO 340 ELSE 350
320 REM- THE DENSITY OF AIR AT 850C =.33 KG/CU M
330 REM- THE VISCOSITY OF AIR AT 850 = 4.5E-05 KG/M-SEC
340 DA=.33 : VA=.000045 : GOTO 380
350 PRINT"INPUT DENSITY OF AIR, KG/CU M";:INPUT DA:PRINT
360 PRINT"INPUT VISCOSITY OF AIR AT DESIRED TEMPERATURE, KG/M-SEC"
370 INPUT VA
380 PRINT
390 PRINT")) Which FBC unit is being modelled ";:INPUT B$:PRINT
400 LPRINT" THE FBC UNIT BEING MODELLED IS "; B$
410 PRINT")) What is the limestone identification ";:INPUT A$:PRINT
420 LPRINT" THE LIMESTONE IDENTIFICATION IS "; A$
430 PRINT")) What is the coal feed rate in KG/H";:INPUT C:PRINT
440 LPRINT" THE COAL FEED RATE,KG/H=";C
450 PRINT")) What is the % SULPHUR in the coal";:INPUT D:PRINT
460 LPRINT" THE % SULPHUR IN THE COAL="; D
470 PRINT")) What is the % CaCO3 of the limestone";:INPUT CA:PRINT
480 LPRINT" THE % CACO3 OF THE LIMESTONE="; CA
490 PRINT")) What is the % MgCO3 of the limestone";:INPUT MG:PRINT
500 LPRINT" THE % MGCO3 OF THE LIMESTONE="; MG
510 PRINT")) What is the bulk density of the LIMESTONE FEED, G/CC?"
520 PRINT"   This density is normally about 1.5 g/cc";:INPUT F:PRINT
530 REM * THE BULK DENSITY IS DETERMINED BY GENTLY POURING A SAMPLE OF
540 REM    * LIMESTONE FEED INTO A TARED GRADUATED CYLINDER
550 LPRINT " THE BULK DENSITY OF THE LIMESTONE FEED, G/CC="; F
```

```
560 PRINT"}} What is the raw limestone particle density, G/CC"
570 PRINT"       This density is normally about 2.5 g/cc";:INPUT P:PRINT
580 LPRINT"THE RAW LIMESTONE PARTICLE DENSITY, G/CC="; P
590 PRINT"}} What is the sulphation capacity (Decimal Fraction)";:INPUT X:PRINT
600 LPRINT"THE SULPHATION CAPACITY, DECIMAL FRACTION="; X
610 PRINT"}} Is the above input correct";:INPUT R$
620 IF R$="Y" THEN 630 ELSE 390
630 PRINT"}} It is necessary to know or to calculate the average particle size "
640 PRINT"   of the limestone. Do you know this value (TYPE 1) or do you wish "
650 PRINT"   to calculate it from a sieve analysis (TYPE 2)";:INPUT R$
660 IF R$="1" GOTO 670 ELSE 700
670 PRINT"}} What is the average particle size of the LIMESTONE FEED (METERS)";:INPUT DP
680 LPRINT"THE AVE PARTICLE SIZE OF LIMESTONE FEED, METERS=";DP
690 GOTO 990
700 DIM SS(10),WT(10),SA(10),SW(10)
710 PRINT"}} How many SIEVES were used, including the PAN";:INPUT N
720 FOR I=1 TO N-1
730 PRINT"}} What is the SIZE in MM, SIEVE ";I;:INPUT SS(I)
740 NEXT I
750 PRINT"Is the above correct";:INPUT R$
760 IF R$="Y" THEN 770 ELSE 710
770 FOR I=1 TO N-1
780 PRINT"}} What is the WEIGHT FRACTION MATERIAL RETAINED on SIEVE";I;
790 INPUT WT(I)
800 NEXT I
810 IF I=N THEN 820
820 PRINT"}} What is the WEIGHT FRACTION MATERIAL RETAINED in the PAN"
830 INPUT WT(I)
840 PRINT"Is the above correct";:INPUT R$
850 IF R$="Y" THEN 860 ELSE 770
860 SW(1)=WT(1)/SS(1)
870 FOR I=2 TO N-1
880 SA(I)=SS(I-1)+SS(I)
890 SW(I)=2*WT(I)/SA(I)
900 NEXT I
910 SW(N)=WT(N)/SS(N-1)
920 ZS=0
930 FOR I=1 TO N
940 ZS=ZS+SW(I)
950 NEXT I
960 DP=1/(1000*ZS)
970 PRINT"}}The CALCULATED MASS AVERAGE PARTICLE SIZE (meters)=";DP;:PRINT
980 LPRINT"}}The CALCULATED MASS AVERAGE PARTICLE SIZE (meters)=";DP
990 PRINT
1000 PRINT"}} What is the STATIC BED HEIGHT (meters)";:INPUT H:PRINT
1010 LPRINT"THE STATIC BED HEIGHT, METERS="; H
1020 PRINT"}} What is the EXPANDED BED HEIGHT (Meters)";:INPUT L:PRINT
1030 LPRINT" THE EXPANDED BED HEIGHT, METERS="; L
1040 PRINT"}} What is the FLUIDIZING VELOCITY, M/SEC";:INPUT U:PRINT
1050 LPRINT" THE FLUIDIZING VELOCITY, M/SEC="; U
1060 PRINT"}} How many NOZZLES are in the disributor plate";:INPUT ND:PRINT
1070 LPRINT"NUMBER OF NOZZELS IN THE DISTRIBUTOR PLATE="; ND
1080 PRINT"}} What is the  AREA OF THE BED in SQ METERS";:INPUT A:PRINT
1090 LPRINT" THE AREA OF THE BED IN SQ METERS="; A
```

```
1100 PRINT"}} Is the above input correct";:INPUT R$
1110 IF R$="Y" THEN 1120 ELSE 1000
1120 S= 1000*C*D/(100*32*60)
1130 PRINT "SULPHUR FEED RATE, S, MOLE/MIN=";S:PRINT
1140 LPRINT"SULPHUR FEED RATE, S, MOLE/MIN=";S
1150 REM * THE QUANTIY OF CALCIUM IN THE BED = VOLUME OF STATIC BED *
1160 REM      BULK DENSITY * A FACTOR OF 1.1 * CACO3 / MOLECULAR WT
1170 B=A*H*F*CA*110
1180 PRINT "QUANTITY OF CALCIUM IN BED, B, MOLE=";B:PRINT
1190 LPRINT"QUANTITY OF CALCIUM IN BED, B, MOLE=";B
1200 PRINT
1210  REM * CALCULATION OF PARTIALLY SULPHATED LIMESTONE DENSITY
1220 REM        BASED ON RAW DENSITY AND ANALYSIS
1230 Z=P*CA/100
1240 RR=P*MG*40/(100*84)
1250 Y=Z*.56+(P-Z-RR)
1260 T=Z*1.36+(P-Z-RR)
1270 PB=X*T+(1-X)*Y
1280 PRINT "CALCULATED DENSITY OF BED MATERIAL=";PB:PRINT
1290 LPRINT"CALCULATED DENSITY OF BED MATERIAL=";PB
1300 NGA=(DP^3)*DA*9.8*(PB*1000-DA)/VA^2
1310 PRINT"THE VALUE OF GALILEO'S NUMBER =";NGA:PRINT
1320 IF NGA<10^5 THEN 1330 ELSE 1340
1330 UMF=.00134*VA*(NGA^.89)/(DP*DA):GOTO 1350
1340 UMF=.0426*VA*(NGA^.682)/(DP*DA)
1350 PRINT "MIN FLUIDIZING VEL, UMF, M/SEC=";UMF:PRINT
1360 LPRINT"MIN FLUIDIZING VEL, UMF, M/SEC=";UMF
1370 V=(L-H)/L
1380 PRINT"VOLUME FRACTION OF BUBBLES IN THE BED =";V:PRINT
1390 REM * FOLLOWING CALCULATES AVE BUBBLE DIA
1400 DBO=.939*(A*(U-UMF)/ND)^.4
1410 DR=SQR(4*A/3.142)
1420 M=.15*L/DR
1430 DBM=1.64*(A*(U-UMF))^.4
1440 IF DR<DBM THEN 1450 ELSE 1460
1450 J=DR-(DR-DBO)*EXP(-M): GOTO 1470
1460 J=DBM-(DBM-DBO)*EXP(-M)
1470 KL=.11/J
1480 PRINT"THE GAS EXCHANGE COEFF, KL=";KL:PRINT
1490 Q=KL*L*V/(U-UMF)
1500 G=A*(UMF+(U-UMF)*(1-EXP(-Q)))*60000'
1510 PRINT "THE EFFECTIVE GAS FLOW RATE, G, L/MIN =";G
1520 LPRINT"THE EFFECTIVE GAS FLOW RATE, G, L/MIN =";G:GOTO 1740
1530 CS$=CHR$(4)
1540 PRINT CS$:RO$=CHR$(1):RF$=CHR$(2)
1550 PRINT RO$
1560 PRINT"* * * THIS PROGRAM CALCULATES LIMESTONE SULPHATION CA/S RATIO * * *"
1570 REM * THE FOLLOWING IS A MODIFIED VERSION OF IRVING JOHNSON'S
1580 REM * "SO2FBI" PROGRAM, REVISION 31 DEC 80
1590 PRINT RF$:PRINT:PRINT:PRINT
1600 PRINT"WHAT IS THE FBC UNIT BEING MODELLED";:INPUT B$:PRINT
1610 LPRINT" THE FBC UNIT BEING MODELLED IS "; B$
1620 PRINT"}} LIMESTONE IDENTIFICATION ";:INPUT A$:PRINT
1630 LPRINT" LIMESTONE IDENTIFICATION IS ";A$
```

```
1640 PRINT")) INPUT SO2 FEED RATE, MOLES/MIN";:INPUT S:PRINT
1650 LPRINT" INPUT SO2 FEED RATE, MOLES/MIN IS ";S
1660 PRINT")) WHAT IS % SULPHUR IN THE COAL";:INPUT D:PRINT
1670 LPRINT" THE % SULPHUR IN THE COAL="; D
1680 PRINT")) INPUT % CACO3";:INPUT CA:PRINT
1690 LPRINT" INPUT % CACO3 OF LIMESTONE ";CA
1700 PRINT")) INPUT QTY OF CALCIUM IN THE BED, MOLES";:INPUT B:PRINT
1710 LPRINT"  QTY OF CALCIUM IN THE BED, MOLES"; B
1720 PRINT")) INPUT EFFECTIVE GAS FLOW, L/MIN";:INPUT G:PRINT
1730 LPRINT" EFFECTIVE GAS FLOW, L/MIN"; G
1740 PRINT")) INPUT A,K,N OF SULPHATION EQN ";:INPUT AA,K2,N:PRINT
1750 LPRINT" INPUT A,K,N OF SULPHATION  EQN ARE "; AA,K2,N
1760 PRINT")) IS THIS DATA FROM THE FB REACTOR OR TGA";:INPUT C$:PRINT
1770 LPRINT" THIS DATA ARE FROM "  ;C$
1780 PRINT")) INPUT SO2 CONC OF TEST";:INPUT P2:PRINT
1790 LPRINT" INPUT SO2 CONC OF TEST IS "; P2
1800 PRINT")) Is the above input correct";:INPUT R$
1810 IF R$="Y" THEN 1820 ELSE 1600
1820 FOR I=1 TO 10
1830 READ Y(I),W(I)
1840 NEXT I
1850 K=K2:P=P2
1860 PRINT:PRINT:PRINT R0$:PRINT A$:PRINT RF$:PRINT
1870 GOSUB 2230:        REM PRINT TITLE
1880 FOR J=2 TO 20
1890 L=0
1900 C=.5*J*S
1910 R=B/C
1920 K1=K*(R^N)
1930 L=L+1
1940 IF L>100 THEN END
1950 Z=0
1960 REM LOOP INSERT
1970 FOR I=1 TO 10
1980 E=K1*(Y(I)^N)
1990 IF E<30 THEN 2020
2000 F=AA
2010 GOTO 2030
2020 F=AA*(1-EXP(-E))
2030 Z=Z+F*W(I)
2040 NEXT I
2050 P1=2.24E+07/G*(S-C*Z/100)
2060 IF ABS(P1-P)<.1 THEN 2140
2070 IF P1>0 THEN 2090
2080 P1=.5*P
2090 P1=(P1+P)/2
2100 P1=SQR(P1*P)
2110 K=K*((P1/P)^N)
2120 P=P1
2130 GOTO 1920
2140 CAS=.5*J
2150 RET=CAS*Z
2160 SC=100*D*.5*J/(CA*32)
2170 PRINT
```

```
2180 PRINT USING " ##.# ";CAS;:PRINT"    ";
2190 PRINT USING "  ##.#### ";Z;RET;SC
2200 LPRINT USING " ##.# ";CAS;:PRINT"    ";
2210 LPRINT USING "  ##.#### ";Z;RET;SC
2220 NEXT J
2230 PRINT "(CA/S)";TAB(12);"UTIL";TAB(22);"RET'N";TAB(35);"KG STONE/KG COAL"
2240 LPRINT"(CA/S)";TAB(12);"UTIL";TAD(22);"RET'N";TAB(35);"KG STONE/KG COAL"
2250 PRINT:PRINT
2260 RETURN
2270 DATA .13779,.388441,.72945,.48113
2280 DATA 1.88834,.218868,3.48143,.8628875
2290 DATA 5.5525,8.58152E-03,8.33015,7.53888E-04
2300 DATA 11.8438,2.82592E-05,16.2792,4.24931E-07
2310 DATA 21.9966,1.83956E-09,29.9287,9.91183E-13
2320 END
```